Cu Electroplating for On-Chip Metallization. An Overview

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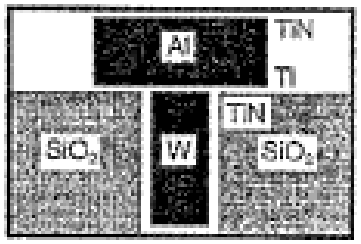
Outline

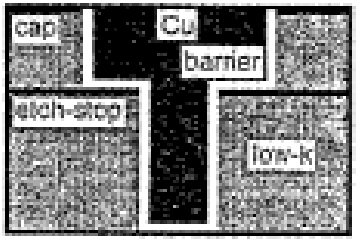
- Cu Damascene Process
- Cu EP mechanism
- Gap fill mechanism and additives
- Bath analysis/replenishment
- Defects and Uniformity
- Films properties
- Conclusions

Cu Damascene Process vs Al



Process Flow
ILD SiO_2 Deposition & Planarization
Photolithography - Via Pattern
Plasma Etch - Via Pattern
Photoresist Strip
TiN Liner Deposition
CVD W Deposition / Etch-back
Ti/Al/TiN Conductor Deposition
Photolithography - Conductor Pattern
Plasma Etch - Conductor Pattern
Photoresist Strip

(a)



Process Flow
Low-k ILD Spin-on & Planarization
Etch-Stop (SiO_2/SiN) Deposition
Photolithography - Via Pattern
Etch-Stop Layer Etch - Via Pattern
Photoresist Strip
Low-k ILD Spin-on
Cap Layer (SiO_2/SiN) Deposition (Optional)
Photolithography - Conductor Pattern
Plasma Etch - Via & Conductor Trench
Photoresist Strip
Cu CMP

(b)

Low K-ILD Deposition and Planarization

Photolithography[a] - via pattern
Photoresist strip
Photolithography[b] - interconnect trench pattern

Photoresist strip

Deposit interconnect metal alloy (e.g., Cu(Mg) or Cu(Al))

CMP

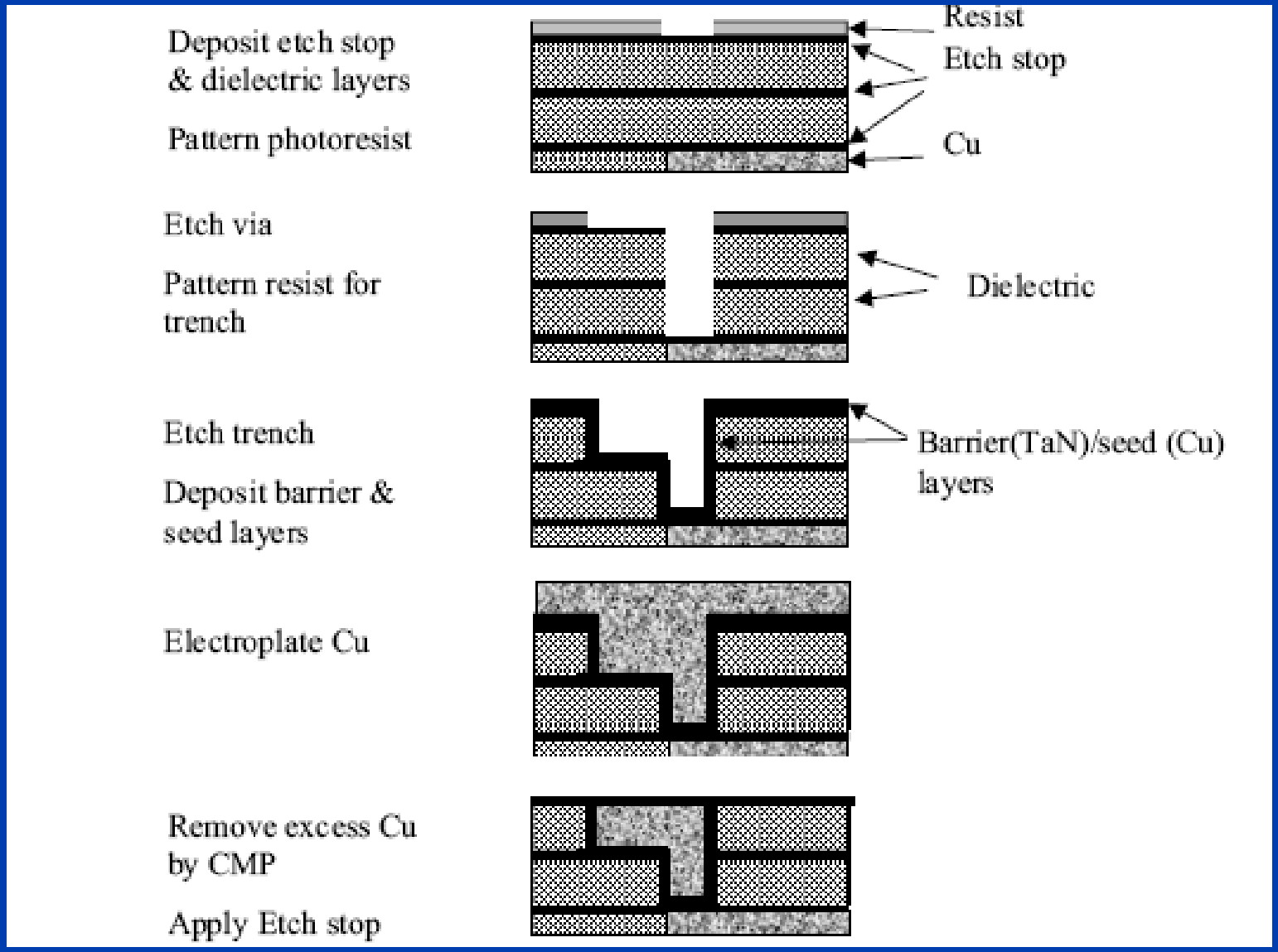
(c)

PVD Ta/TaN barrier + PVD Cu seed dep + Cu EP

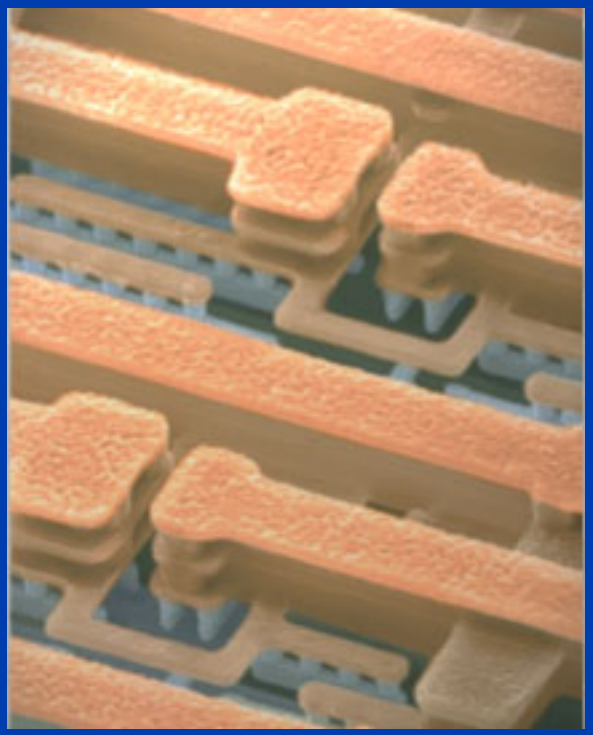
Comparison of a variety of processes: (a) a W/Al, (b) encapsulated Cu, and (c) Cu alloy schemes. Note in all cases assumption is made that deposition processes will achieve the via fill desired.

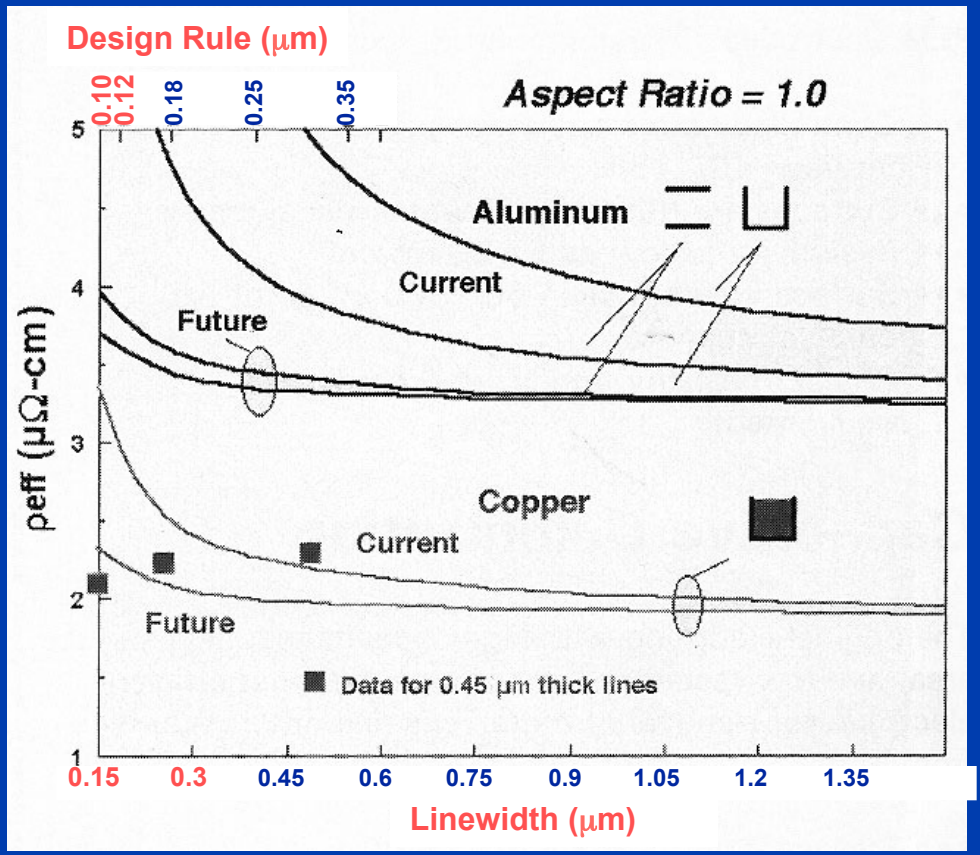
Cu replaced Al as on-chip metallization due to higher electromigration resistance (10x+) and lower resistivity (30%+) as well as cost reduction (about 20%)

Cu Dual Damascene Process



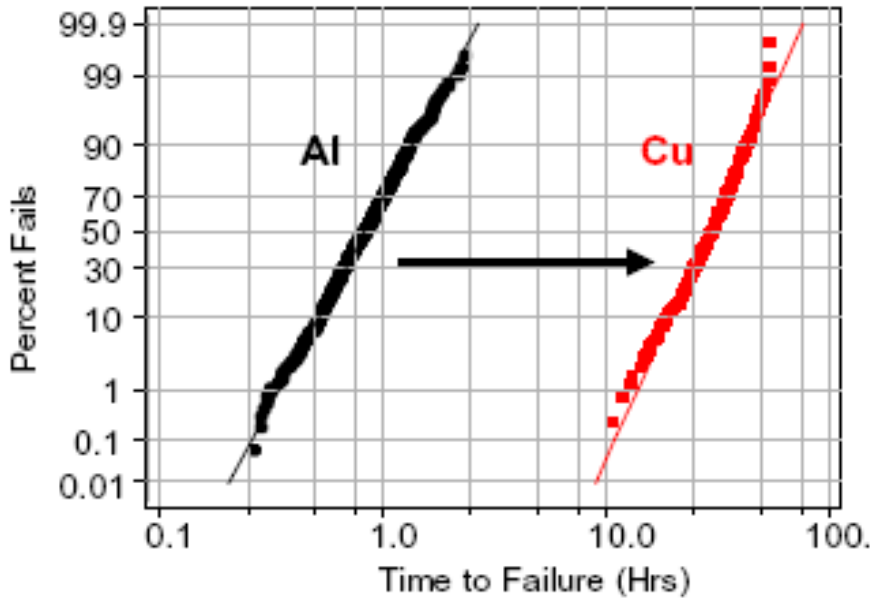
Copper On-Chip Interconnections

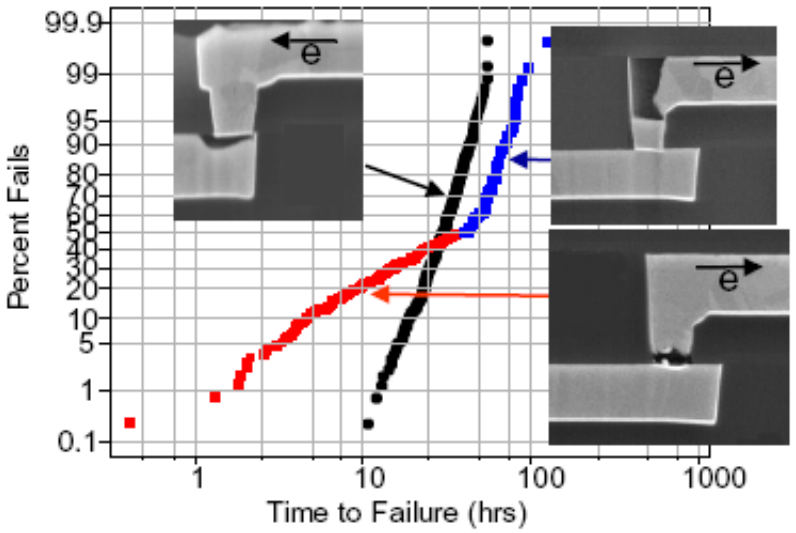




Cu RC is 30%+ lower than that of Al interconnects

Cu Electromigration





Cu EM resistance is 100x higher than that of Al interconnects

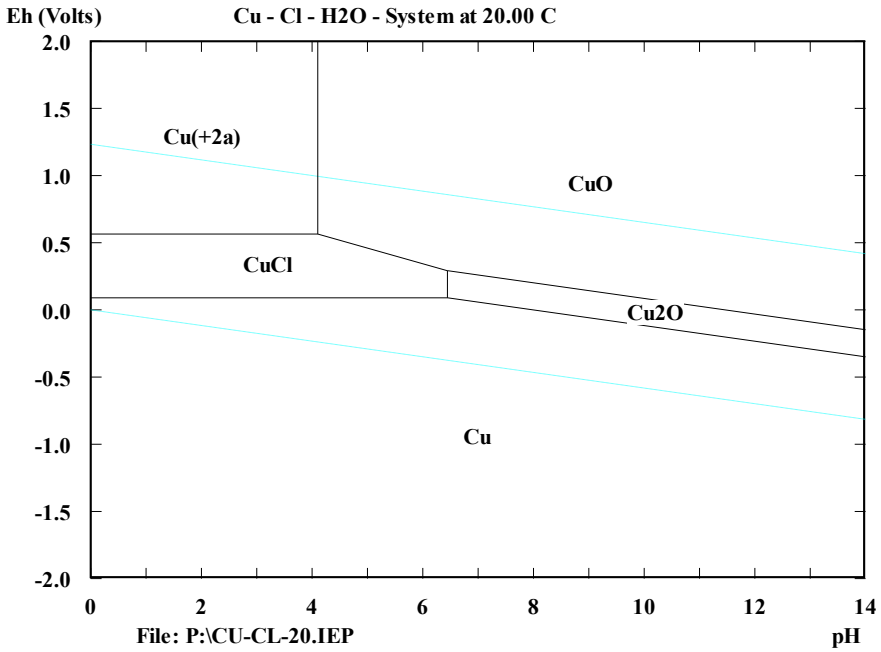
Cu EP Mechanism

- Mechanism at the anode
  - $Cu \rightarrow Cu^{+} + e^{-}$ (fast)
  - $Cu^{+} \rightarrow Cu^{2+} + e^{-}$ (slow)
- Rate limiting step is oxidation of Cu^{+} to Cu^{2+}
- Accumulation of Cu^{+} is possible and CuCl precipitation is likely in presence of Cl^{-}

- Mechanism at the cathode
  - $Cu^{2+} + e^{-} \rightarrow Cu^{+}$ (slow)
  - $Cu^{+} + e^{-} \rightarrow Cu$ (fast)
- Rate limiting step is reduction of Cu^{2+} to Cu^{+}
- Cu^{+} does not accumulate and CuCl precipitation is unlikely in presence of Cl^{-}

Cu EP Mechanism: Anode

Pourbaix diagram for Cu-Cl-H_2O system



- Copper oxides are unstable under acidic conditions in the presence of Cl^-
- When Cl^- is present, Cu(I) can be stable in the form of a *CuCl film*
- Stability of CuCl film is affected by changes in $[Cu^+]$ or $[Cl^-]$ and pH, due to:
  - different electrolyte
  - different processing conditions
- Cu(I) in CuCl can be oxidized by dissolved O_2

$$4CuCl + O_2(a) + 4OH^- \rightarrow 4CuO + 4Cl^- + 2\,H_2O \qquad \Delta G = -83 \text{ kcal/mole}$$

Cu EP Mechanism at the Anode

- Solubility product constants (K_{sp}) of least soluble copper salts:

$CuCl\,(s)$	$\leftrightarrow Cu^{+}\,(aq) + Cl^{-}\,(aq)$	$K_{sp} = 1.7 \bullet 10^{-7}\ M^2$
$Cu_3(PO_4)_2\,(s)$	$\leftrightarrow 3\ Cu^{2+}\,(aq) + 2\ PO_4^{3-}\,(aq)$	$K_{sp} = 1.4 \bullet 10^{-37}\ M^5$
$CuSO_4\,(s)$	$\leftrightarrow Cu^{2+}\,(aq) + SO_4^{2-}\,(aq)$	$K_{sp} = 2.3\ M^2$

- Cupric sulfate is much more soluble than cuprous chloride or cupric phosphate

Cu EP Mechanism: Anode

- **Ion Chromatography (IC) and ICP-atomic emission spectroscopy of Cu anode films**

Sample	IC				ICP
	Cl (μg/ml)	SO_4^{2-} (μg/ml)	Cl/SO_4^{2-}	HPO_4^- (μg/ml)	P/Cu
1	214	4969	1 : 23	N/A	1 : 81
2	22.8	507	1 : 22	0.99	1 : 72
3	135	5.5	24 : 1	1.03	1 : 85

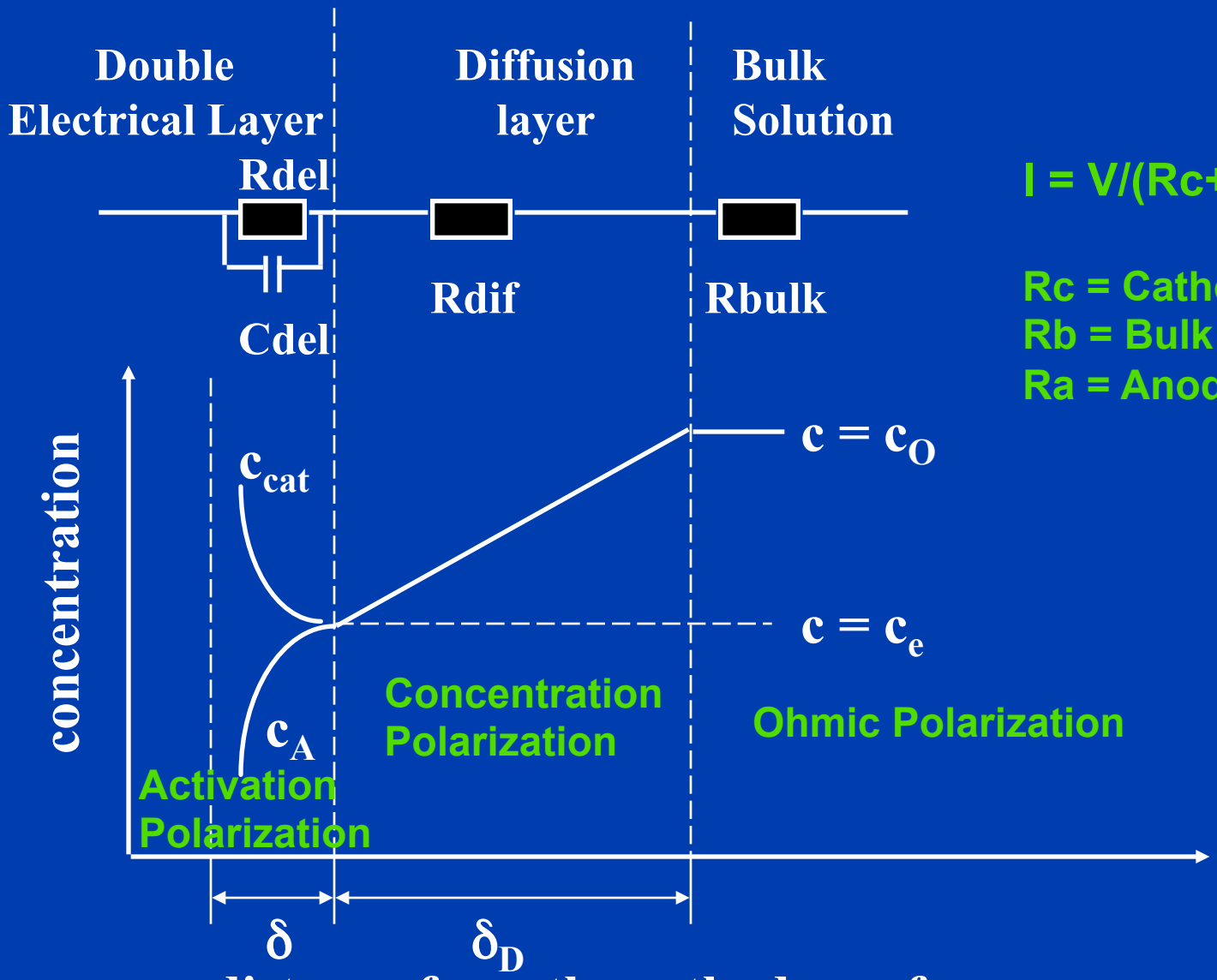
- IC results show Cl/SO4 ratio in all three samples are much higher than Cl/SO4 ratio in plating bath (1:1000)

  → strong indication of CuCl in the anodic film

Cathodic Polarization

- Concentration Polarization
- Activation Polarization
- Ohmic Polarization
- Crystallization Polarization

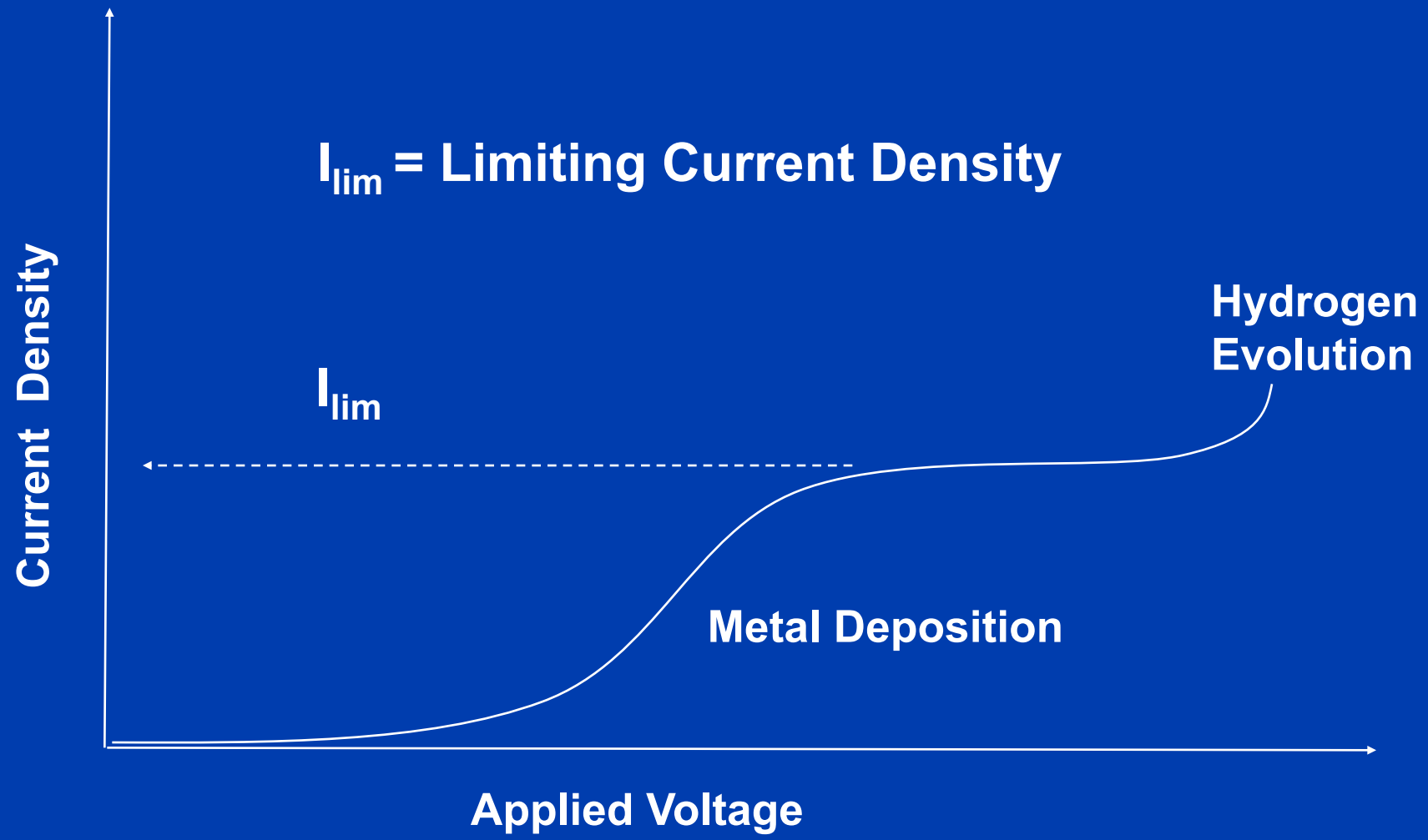
Cu EP Mechanism at the Cathode



I = V/(Rc+Rb+Ra)

Rc = Cathodic Resistance
Rb = Bulk Resistance
Ra = Anodic Resistance

Cathodic Polarization Curve



Electrochemical Equations

- **Faraday Law**

$$W = ItA_w/nF$$

- **Fick's Law**

$$I_{lim} = (nFDC)/\delta$$

- **Tafel's Law**

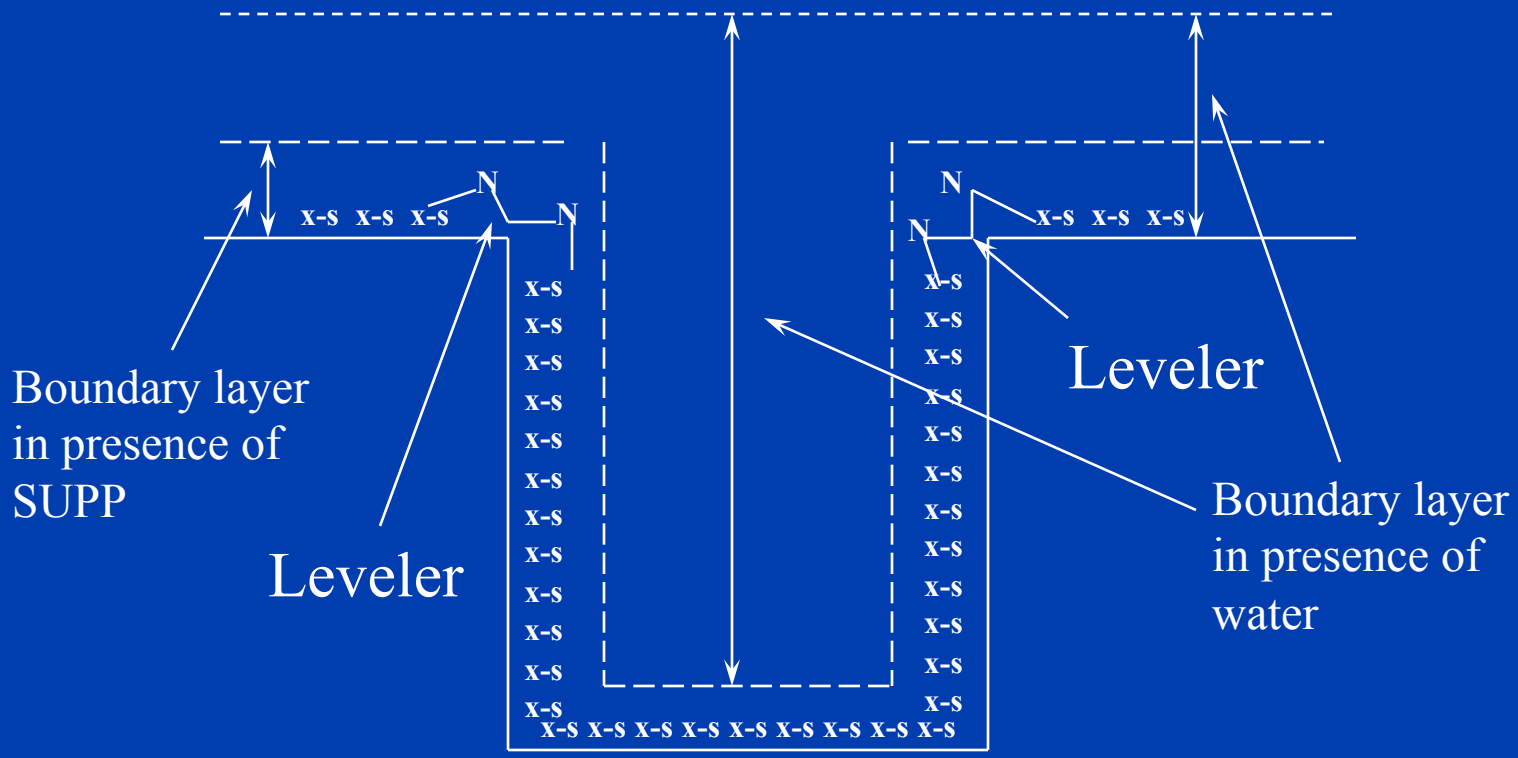
$$I = AExp(B\acute{\eta})$$

- **Butler-Volmer Equation**

High-Field Approximation: $i = i_oExp[(1-\beta)\acute{\eta}F/RT)$

Low-Field Approximation: $I = i_o(F\acute{\eta}/RT)$

Cu EP Mechanism: Cathode

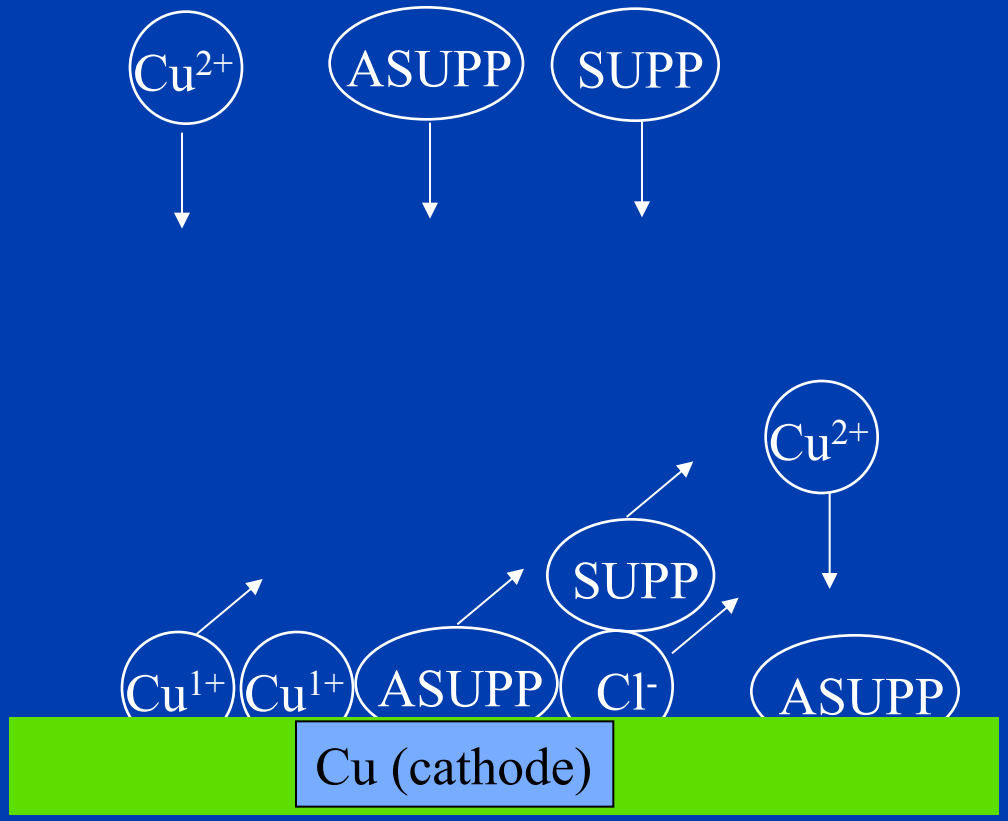


x-s is Brightener

Cu EP Mechanism - Additives

- **Wetting agent - strong suppressor (SUPP)**
  - converts stationary water boundary layer of uneven thickness into a water/P.E. matrix boundary layer on even thickness
  - Suppress/decrease Cu deposition rate acting with Cl
  - Examples: polyethers R-O-[C_nH_{2n}]-OH
- **Brightner - anti-suppressor (ASUPP)**
  - negatively charged additives which reduces effect of suppressors and facilitate Cu2+ to Cu+ reduction.
  - Examples: mercapto alkylsulfonic acids
- **LEVELER - weak suppressor**
  - produces deposits relatively thicker in small recess and relatively thinner on the peaks
  - protonates and adsorbs preferentially near the most negatively charged sites of the cathode.
  - forms complex with Cu and slow down the copper deposition rate
  - Examples: quaternary polyimines, polyamides

Cu EP Mechanism - Additives

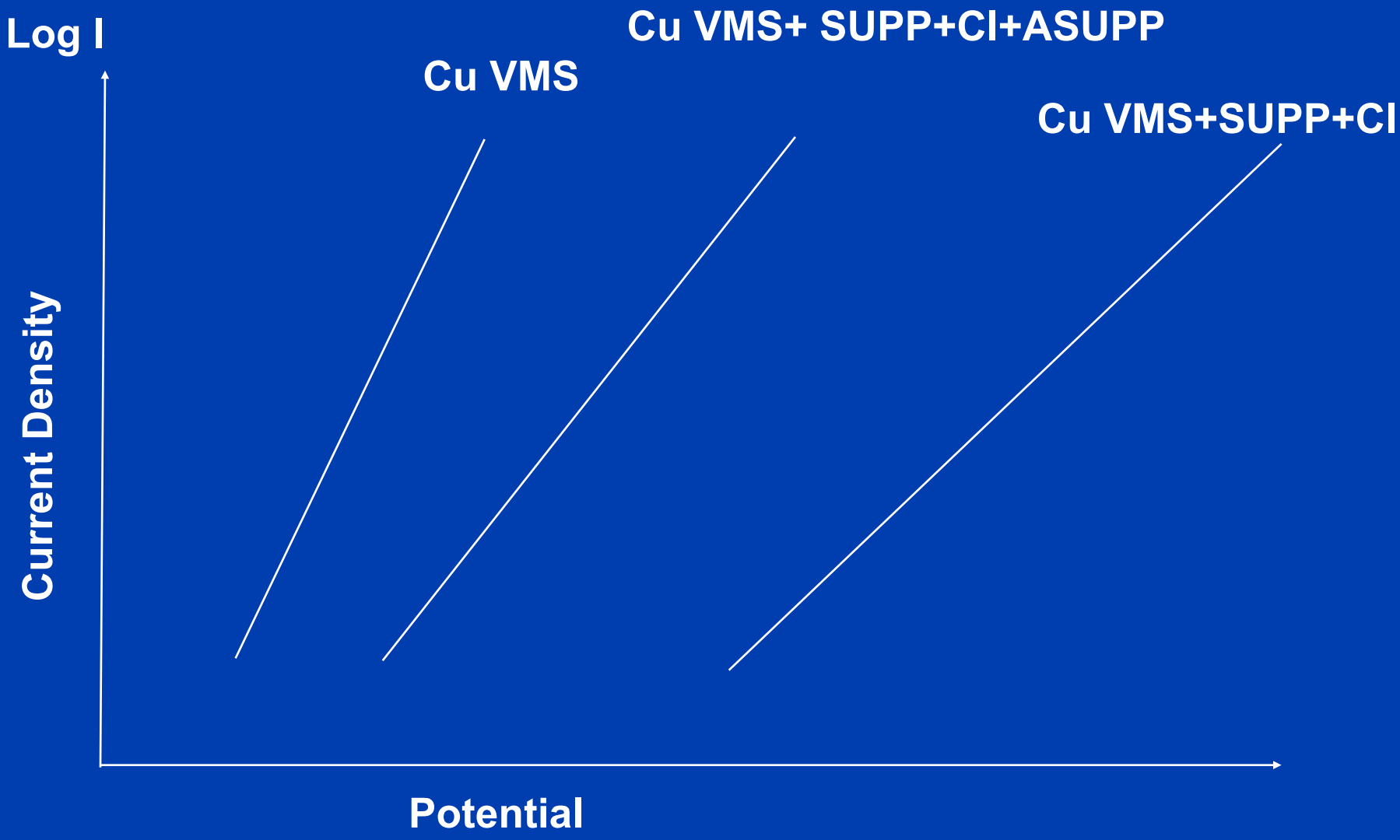


- Model includes:
  - Mass-transport of individual species
  - Interactions among additive species on cathode surface
  - Consistent multi-species adsorption - desorption kinetics

Effect of Additive on Polarization Resistance

- Suppressor – No effect on polarization resistance
- Suppressor + Chloride – Increase polarization resistance
- Accelerator + Suppressor + Chloride – Decrease of the polarization resistance

Tafel Plots


Log I
Cu VMS+ SUPP+Cl+ASUPP
Cu VMS
Cu VMS+SUPP+Cl
Current Density
Potential

"Superfill" Cu EP mechanism

$Cu^{2+} + e = Cu^{+}$ (slow)

$Cu^{+} + e = Cu$ (fast)

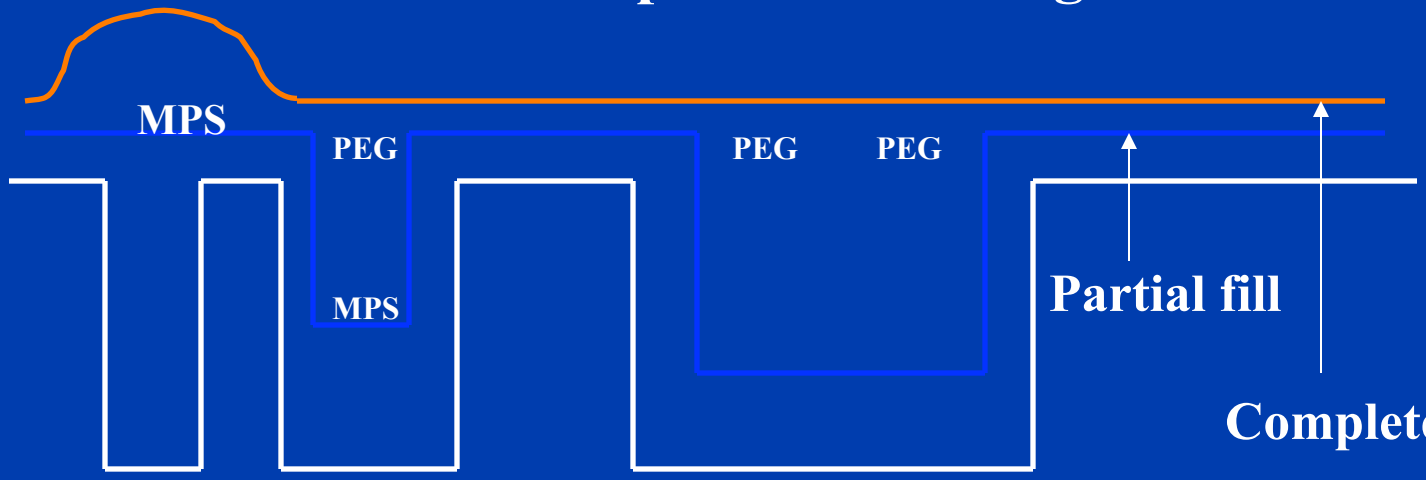
$SPS^{2-} + e = 2MPS^{-}$ (ASUPP-mercaptopropansulfonate)

MPS Diffusion gradient formed in features

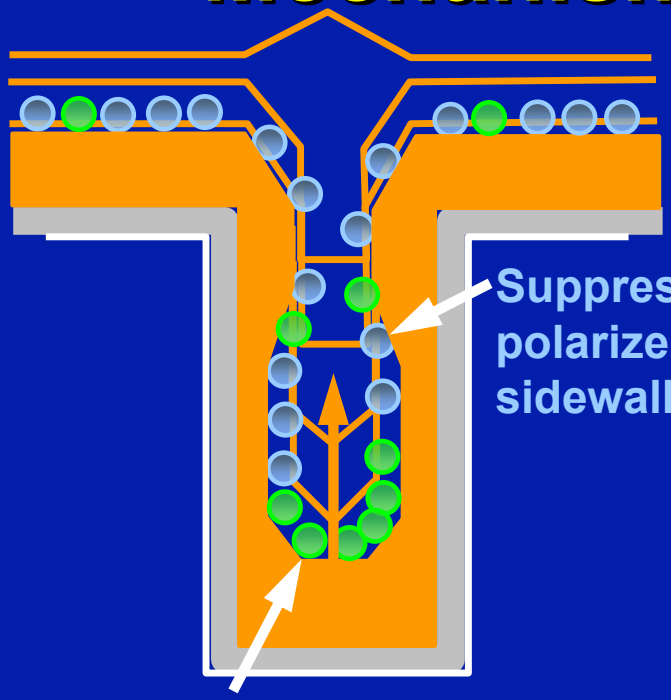
MPS adsorbed on Cu surface

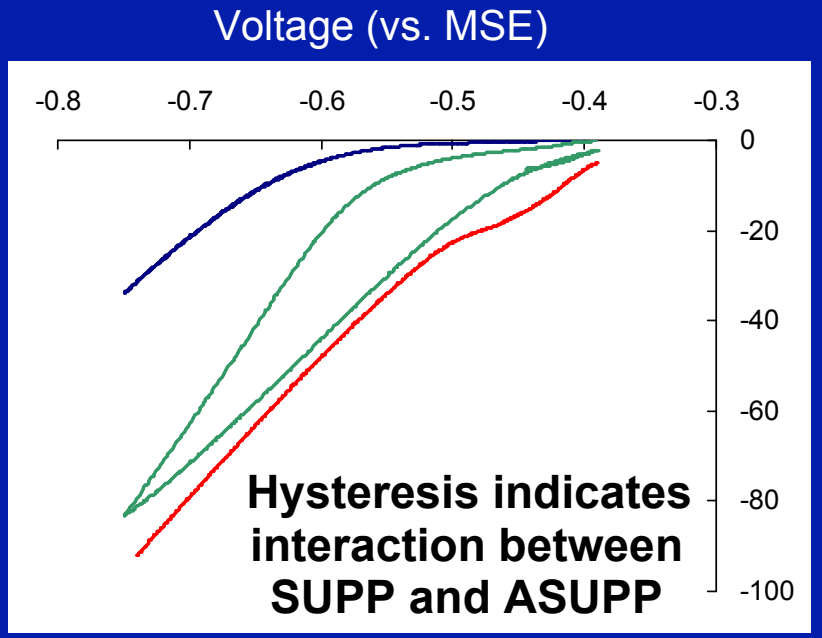
Cu(I)MPS complex accelerate plating - "superfill"

PEG & Cl complex suppress deposition at top openings and flat surface to produce leveling



Mechanism of 'Bottom-up' Fill





- **Factors that impact Bottom-up Fill rate**
  - **Additives (Suppressors, Levelers)**
  - **Plating current density (plating rate)**
  - **Feature-scale diffusion boundary layer (agitation)**

Ref. T. P. Moffat *et al.*, *Electrochem. Solid-State Lett.*, **4**, C26 (2001)

Summary of Superfill Mechanism

Additives	MW	Diffusion Rate	Adsorption Rate	Displacement
Accelerator (S-R)	Small	Fast	Slow	By Leveler on "Humps"
Suppressor (R-O) + Cl	High	Slow	Fast	By Accelerator on the bottom of features
Leveler (N-R)	High	Slow	Need High E	

Mechanisms:

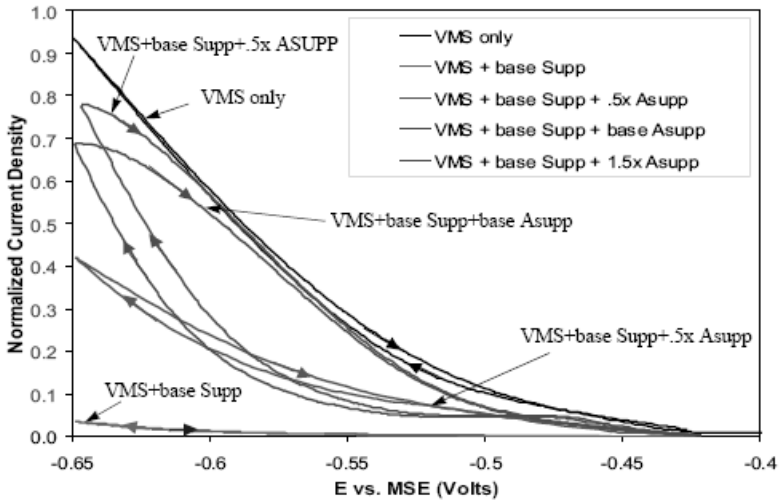
-Gradient of additives in the features due to delta in diffusion vs adsorption rate

-Curvature enhanced mechanism (increase of accelerator concentration due to curvature)

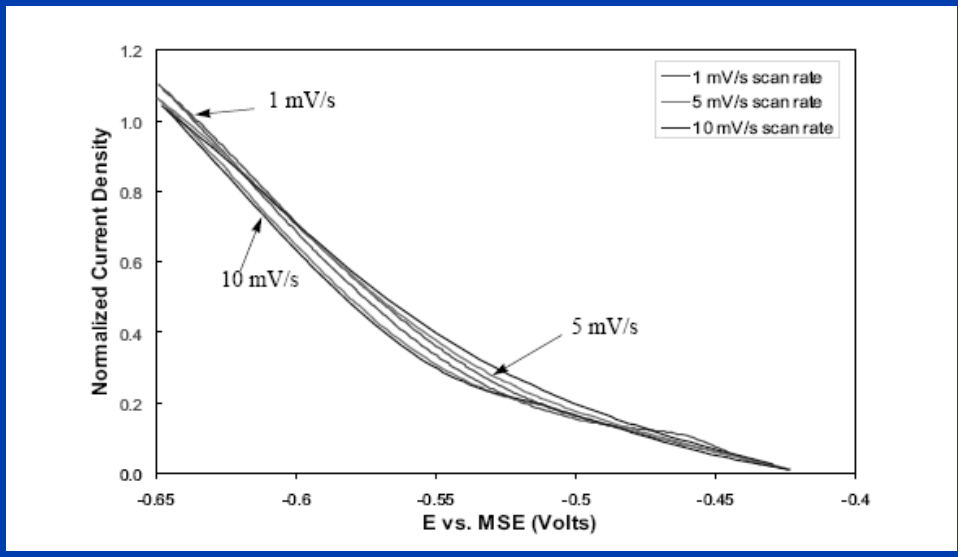
-Complexing of accelerator with Cu+ (facilitate rate limiting reaction);

-Complexing of leveler with Cu2+ (make it rate limiting reaction)

LSV in Cu Plating Bath

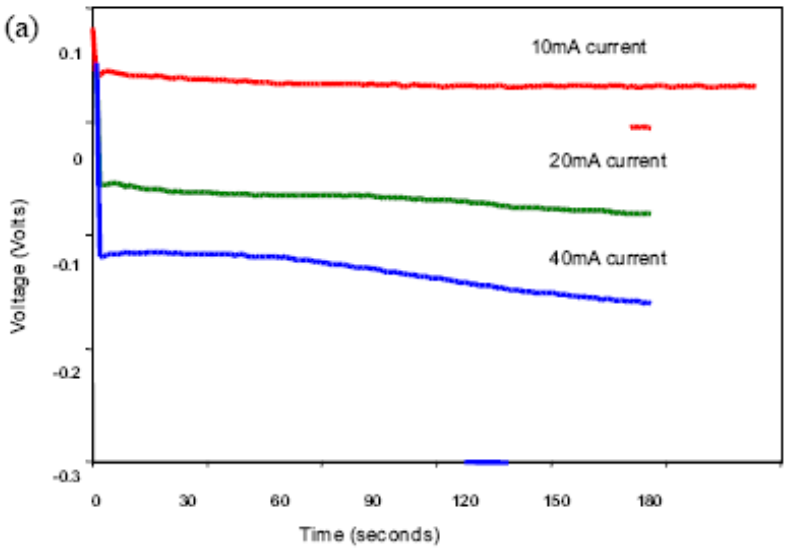


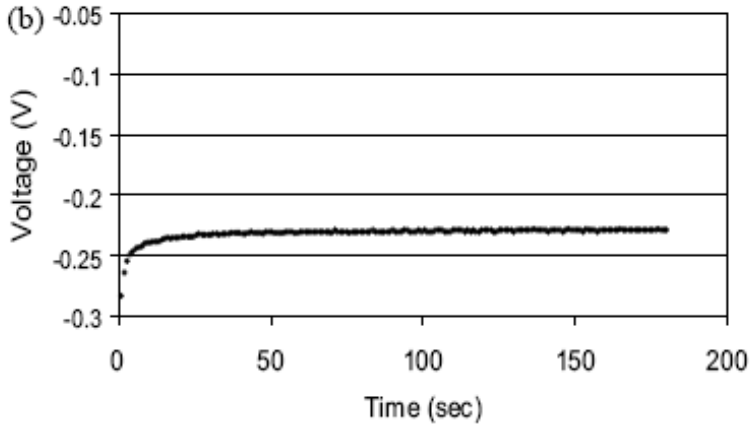
ASUPP and SUPP in the Bath (hysteresis on LSV)



ASUPP in the Bath (no hysteresis on LSV)

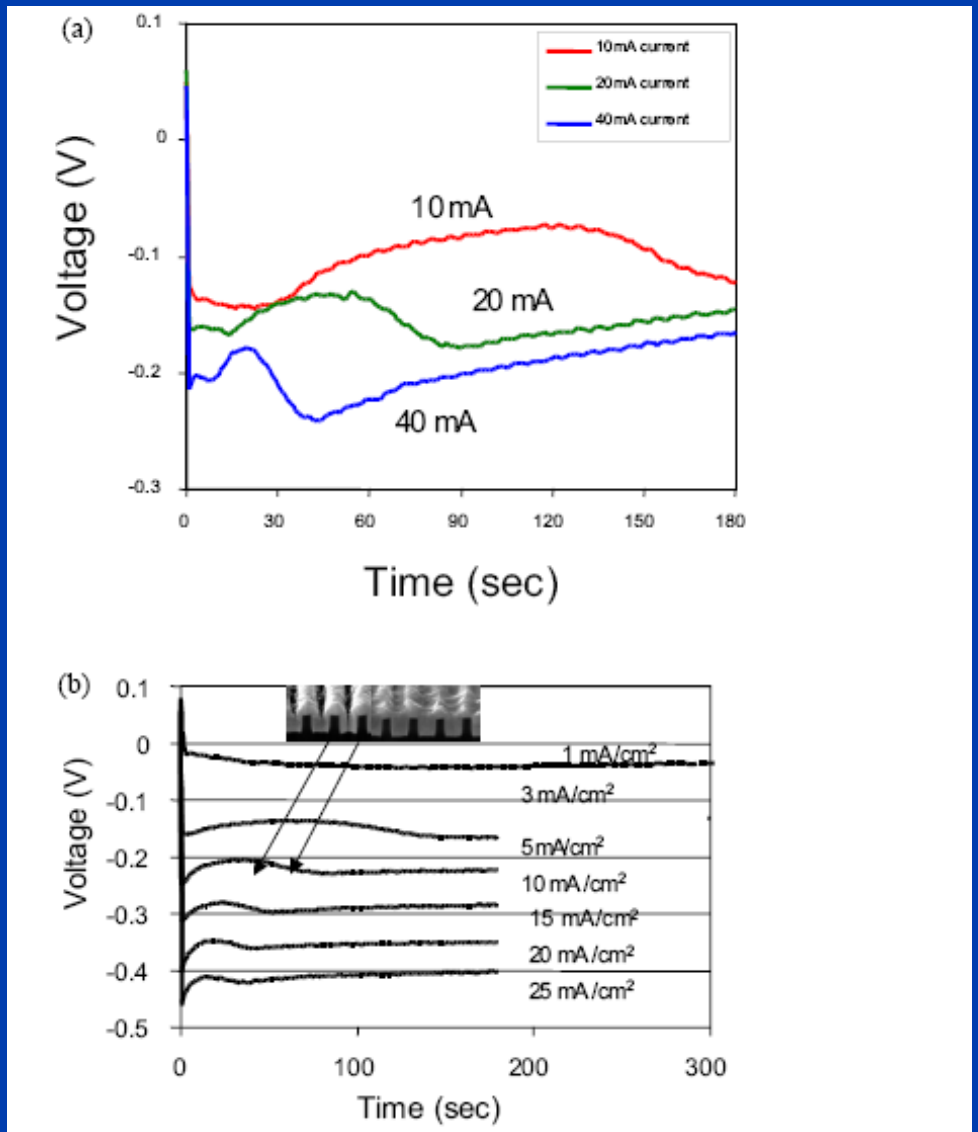
Galvanostatic Cu deposition





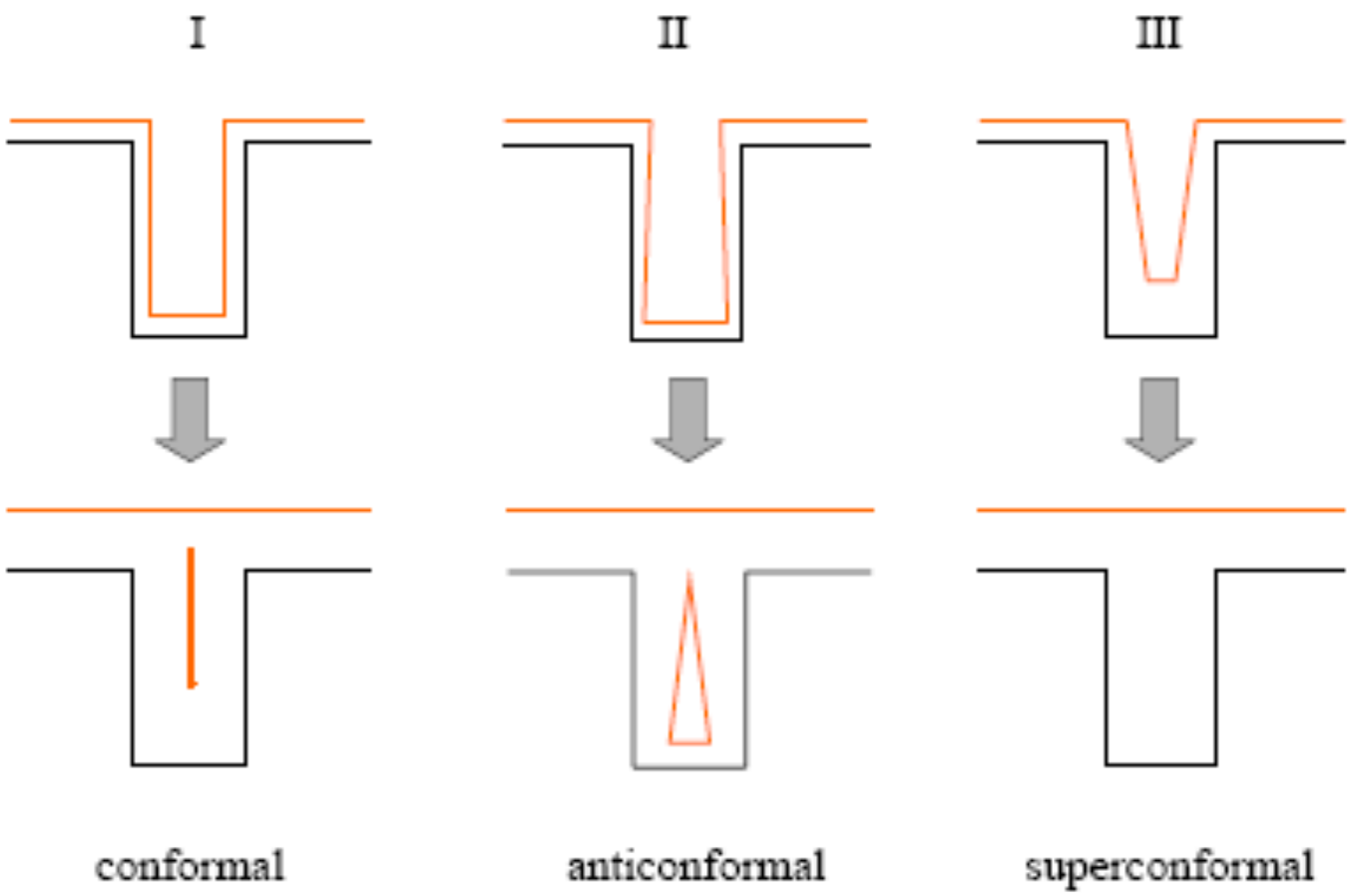
Cathodic potential response as a function of time during galvanostatic copper deposition in (a) high acid, and (b) low acid electrolytes containing additives (ASUPP, SUPP and Leveler) on blanket wafer surfaces at different current densities.

Galvanostatic Cu deposition

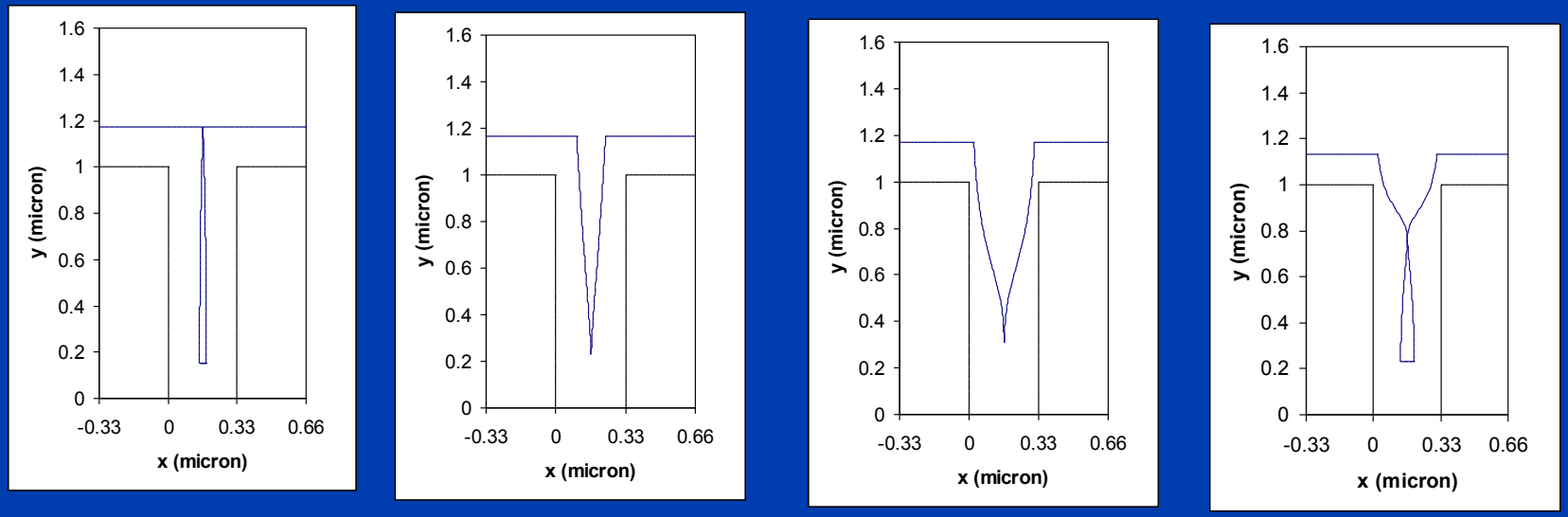


The change of polarization potential with plating time during galvanostatic Cu electroplating onto patterned wafers at different current densities in (a) high acid and (b) low acid electrolytes containing additives (ASUPP, SUPP, and Leveler).

Gap-fill Modes of ECD Cu



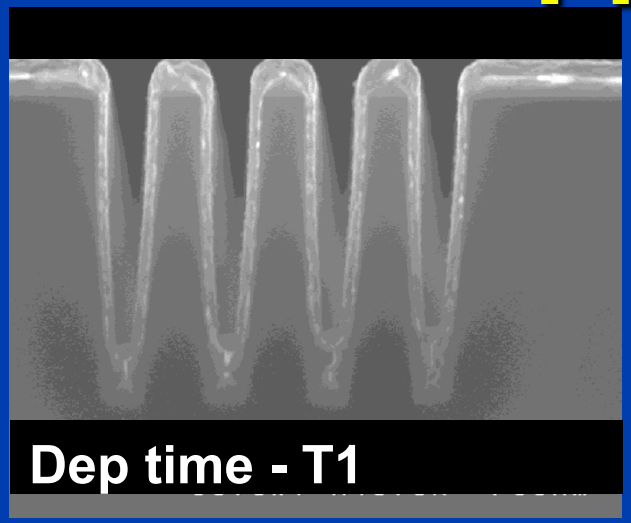
Integrated Electroplating Modeling

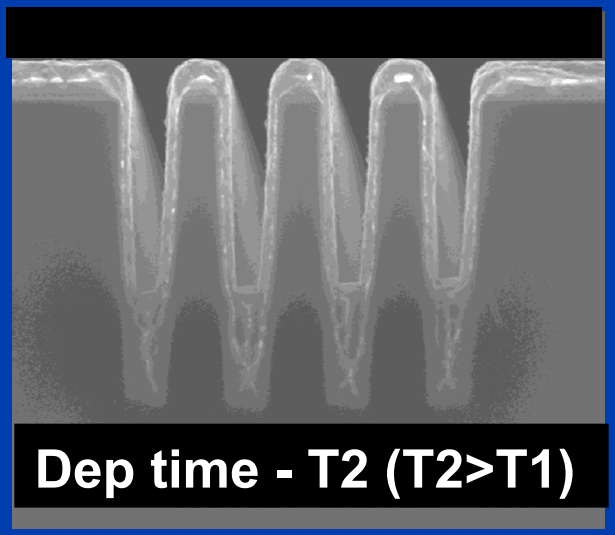


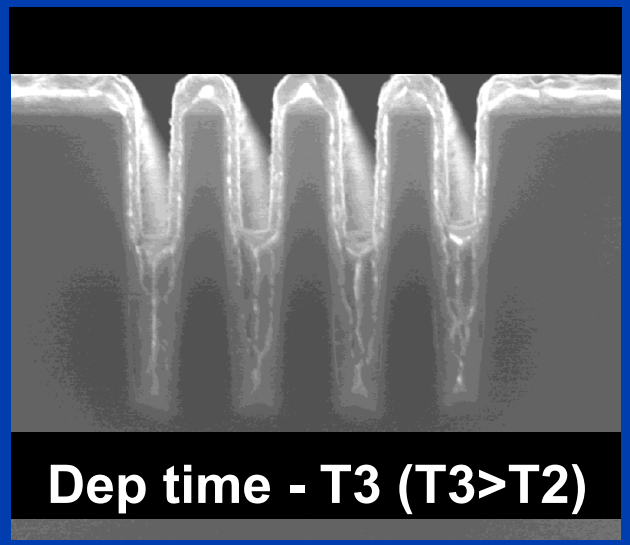
Decreasing [SUPP]

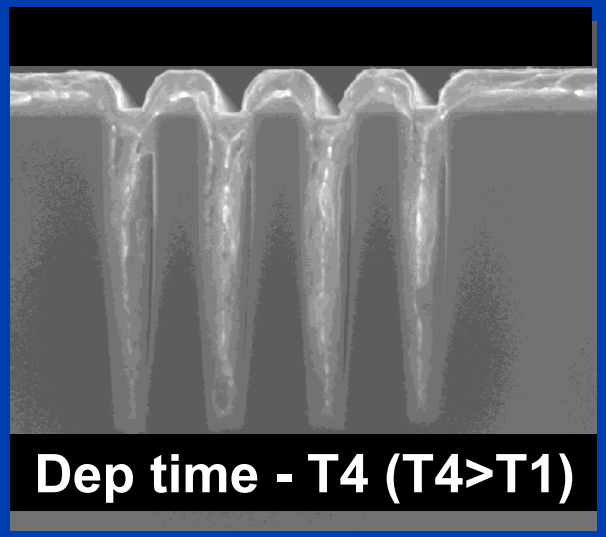
- Shape-evolution model, based on boundary-element method (BEM), was used to study gap-fill properties
- Simulation results show that conformal deposition with seam formation has been observed at high suppression level and center voids have been found at low suppression level

Demonstration of “Super-Fill”

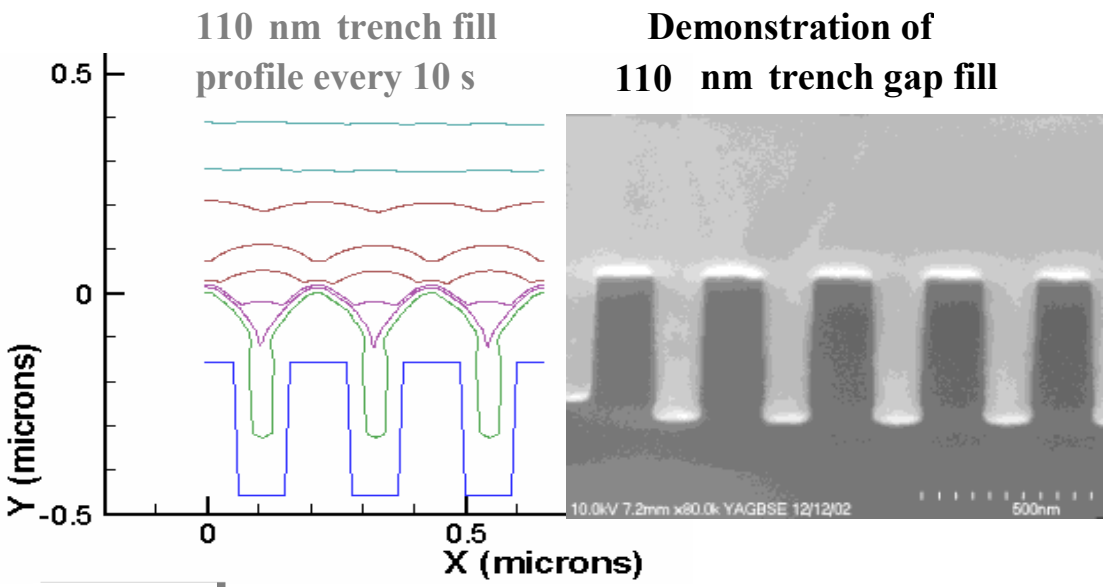




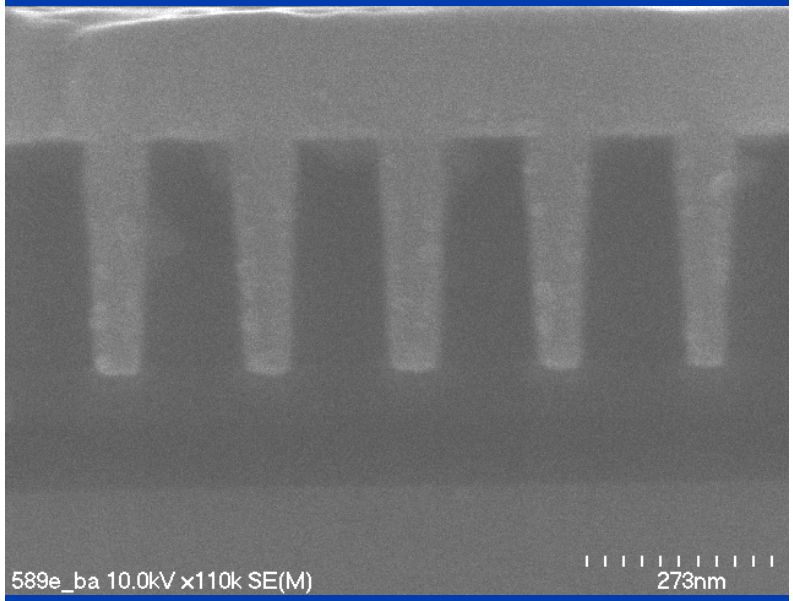




Gap Fill and Cu EP Superfill



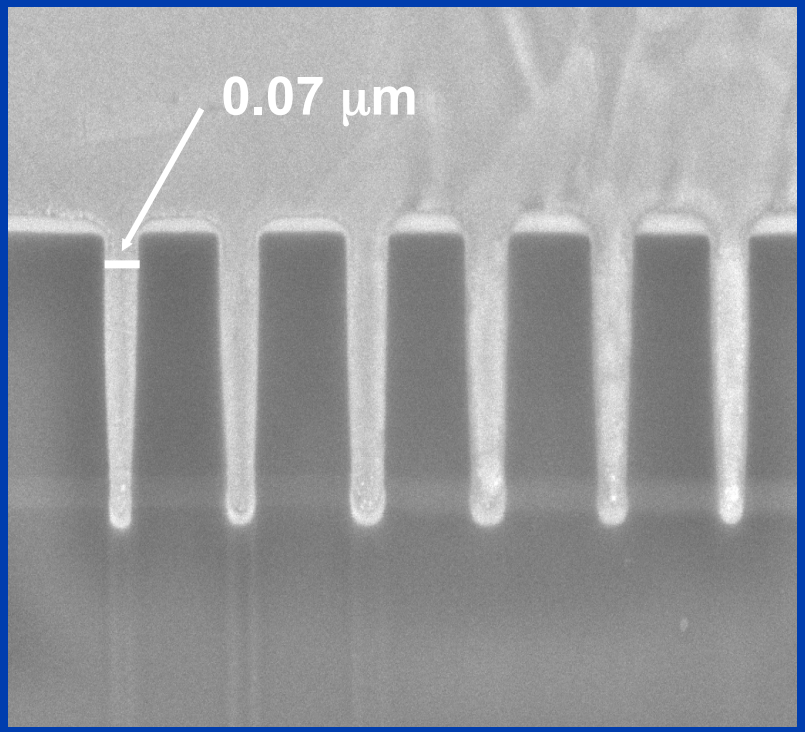
Shape evolution modeling and gap fill capability

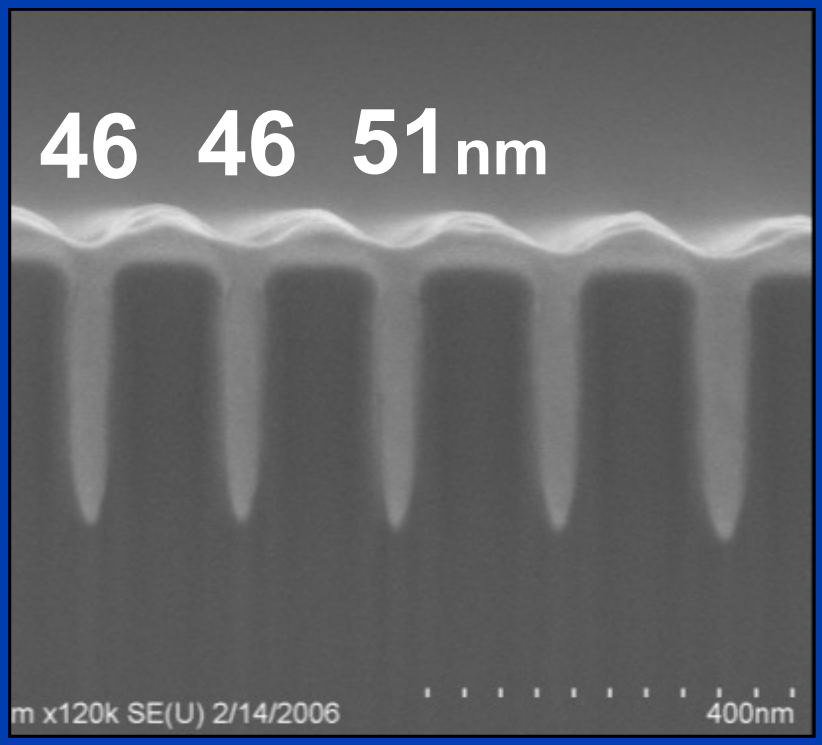


Sub 100 nm Via Fill

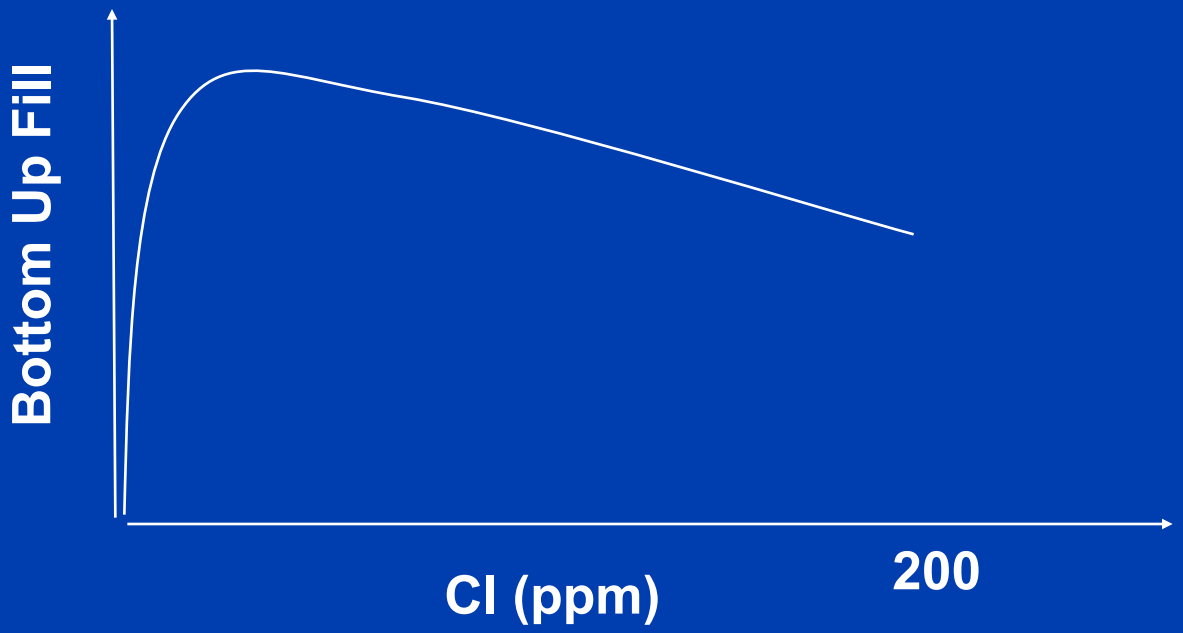
Demonstration of complete gap fill of sub 100 nm trenches and vias

Demonstration of EP fill capability



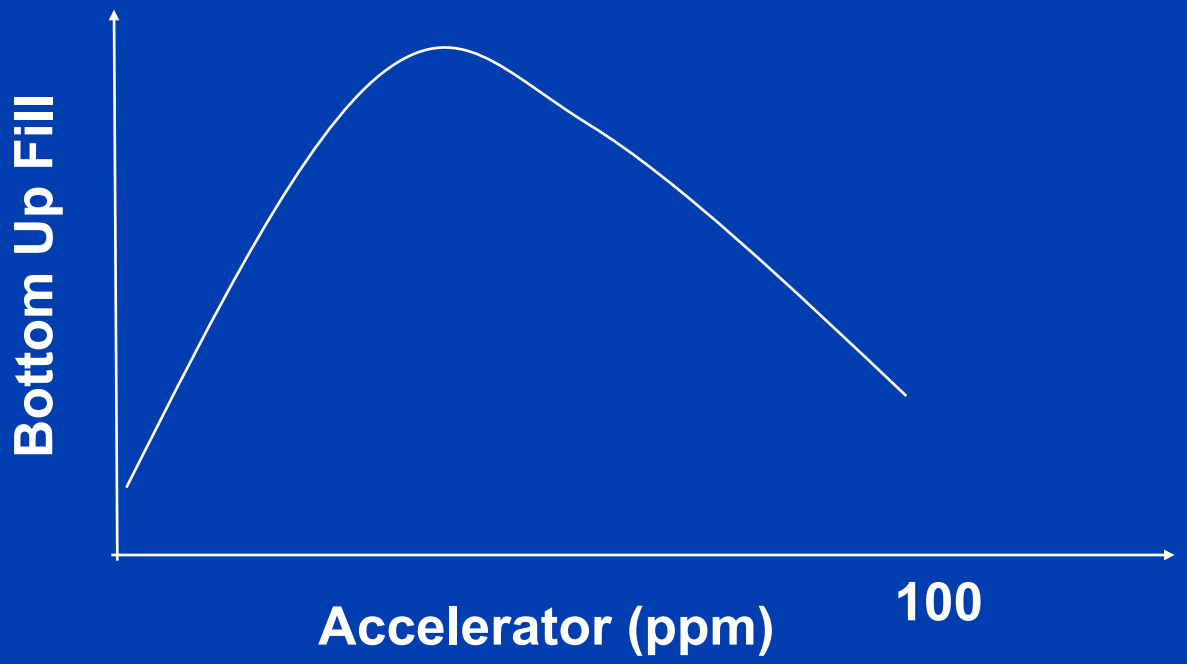


Process Window – Cl concentration



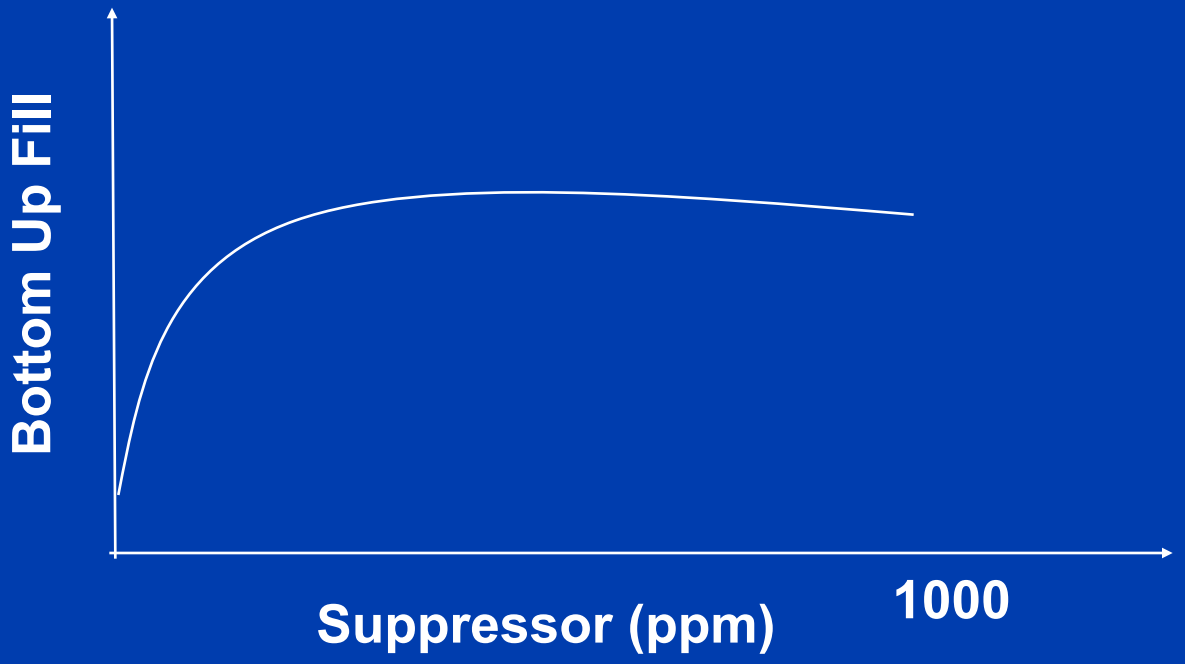
1. Fill has lower bottom up fill rate with no (little(chloride in the bath)
2. Superfill is accelerated at 30 – 100 ppm of Cl in the bath
3. Excess Cl degrade fill and increase Cl level in the film

Process Window – Accelerator Concentration



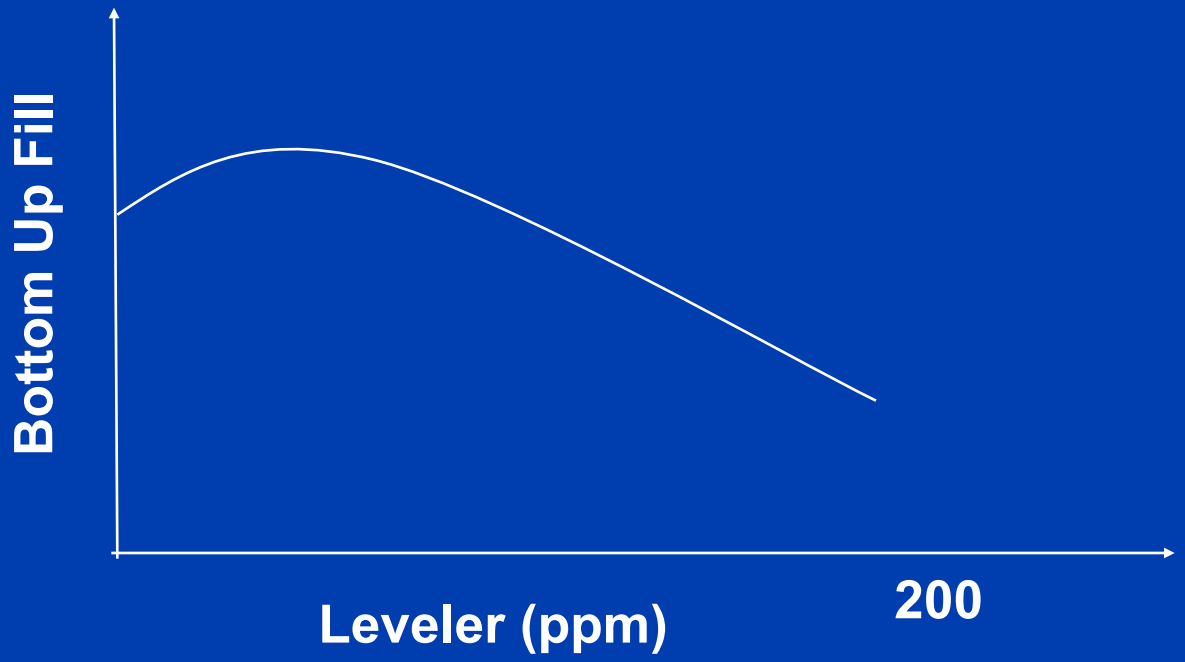
1. Bottom up fill rate is low with No (little) accelerator in the bath
2. Superfill is accelerated at 5 – 100 ppm of accelerator in the bath
3. Excess accelerator degrades fill and increase S level in the film

Process Window – Suppressor Concentration



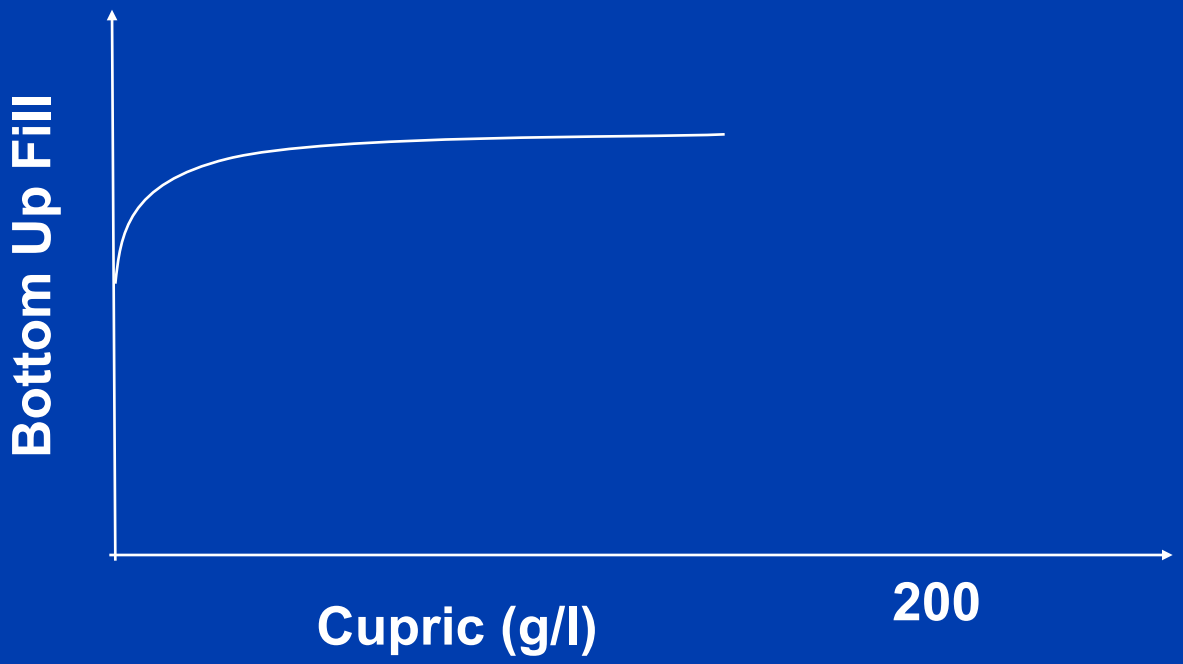
1. Bottom up fill rate is low with No (little) suppressor/Cl in the bath
2. Suppression reaches saturation at 50 – 200 ppm level of suppressor
3. Very high suppressor does not degrade fill (except causing TOC increase and bath foaming)

Process Window – Leveler Concentration



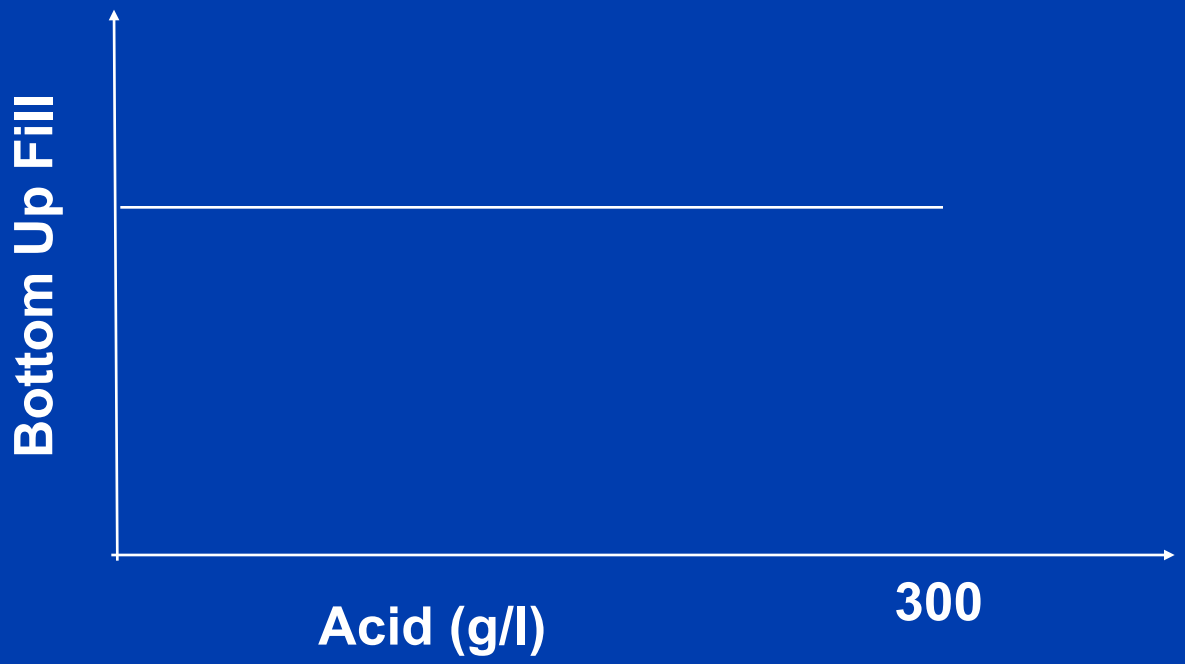
1. Optimized leveler concentration increases fill due to additional suppression
2. Very high leveler concentration degrade superfill

Process Window – Cupric Concentration



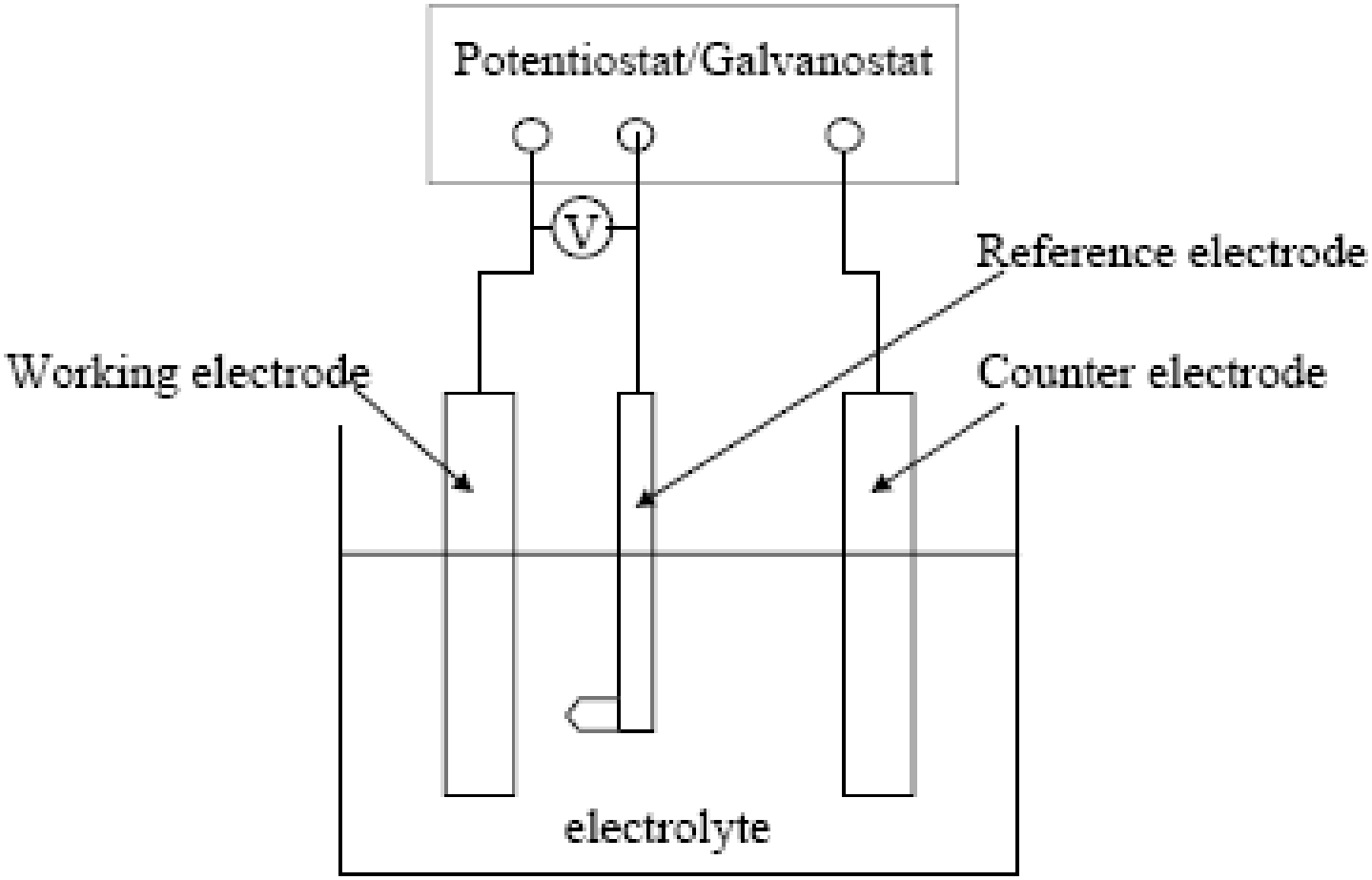
1. Low cupric ion concentration (<10 g/l) degrade fill (diffusion limitation)
2. High cupric ion concentration can cause Cu crystals build up (>80 g/l)

Process Window – Acid Concentration

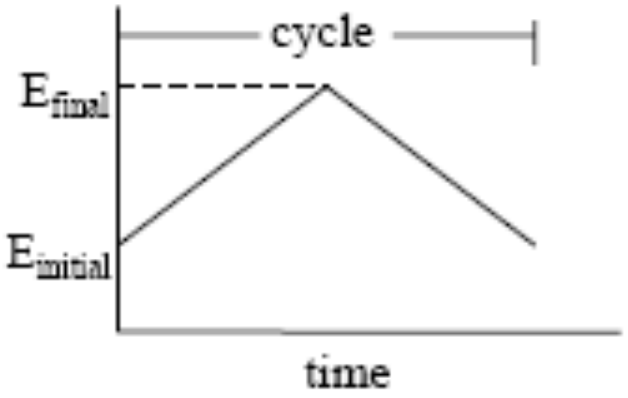


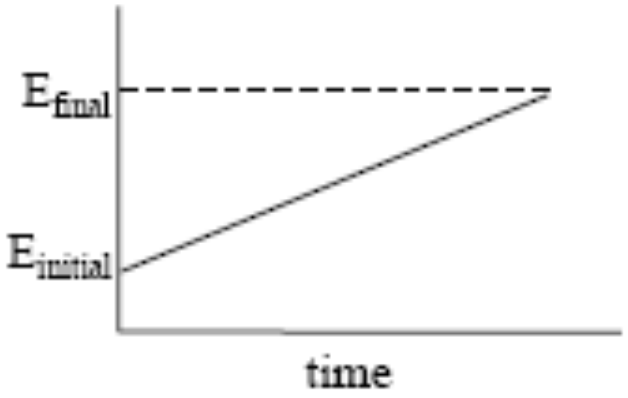
1. Acid (sulfuric) does not degrade fill at 10 – 250 g/l
2. Low acid improves within wafer uniformity

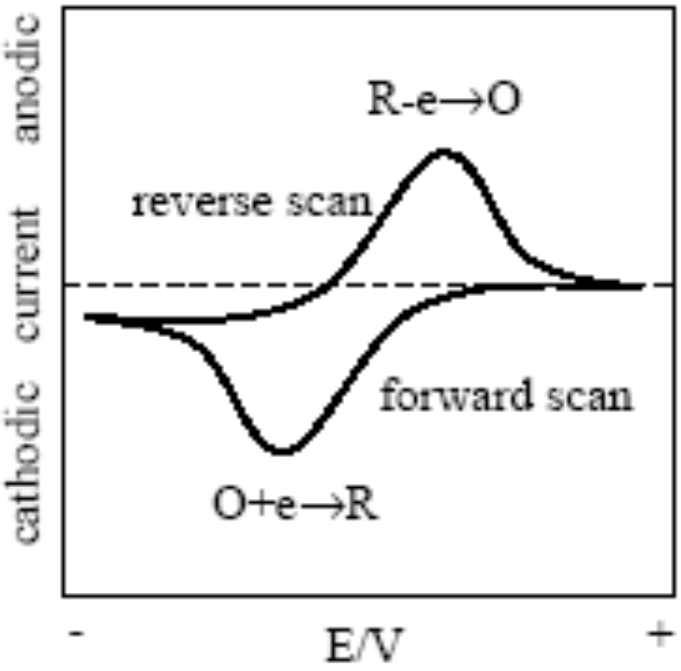
Electrochemical Measurement Set-up

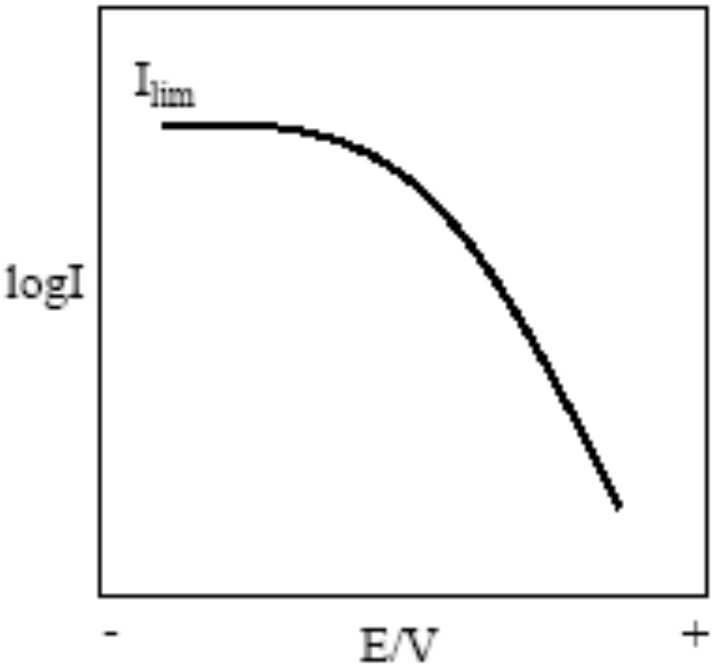


Cyclic and Linear Voltammetry

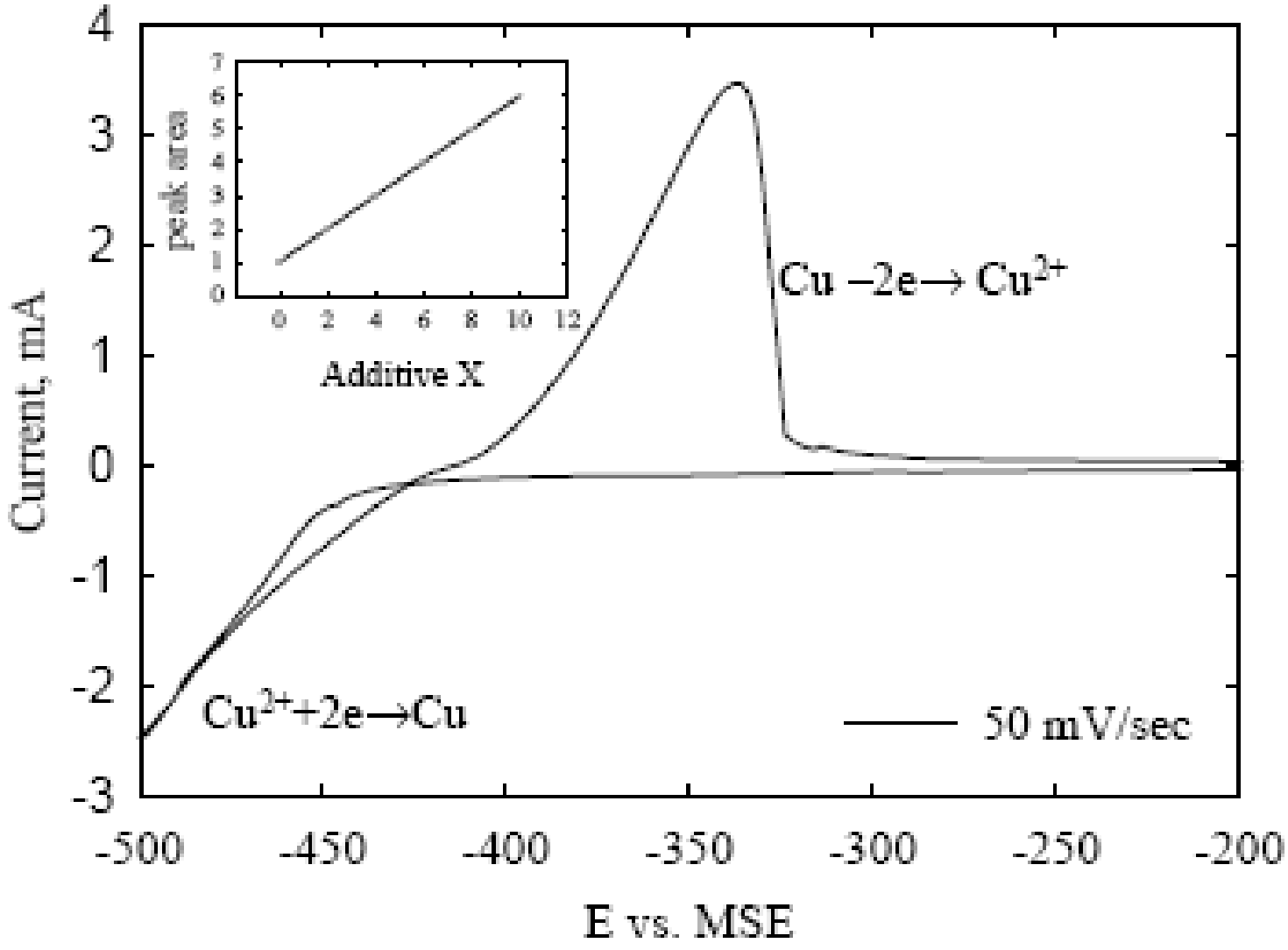




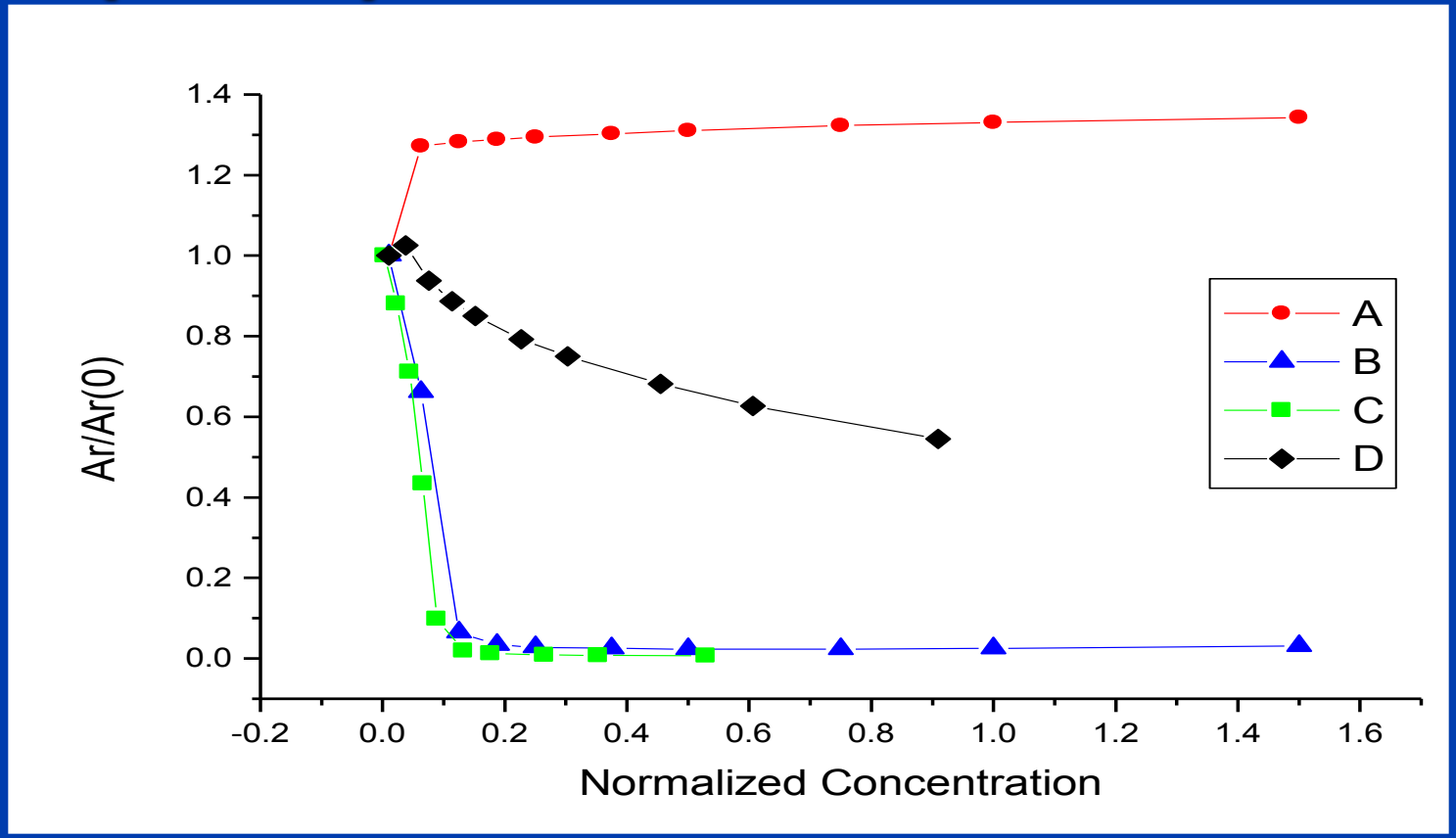




Cyclic Voltammetry Stripping (CVS)

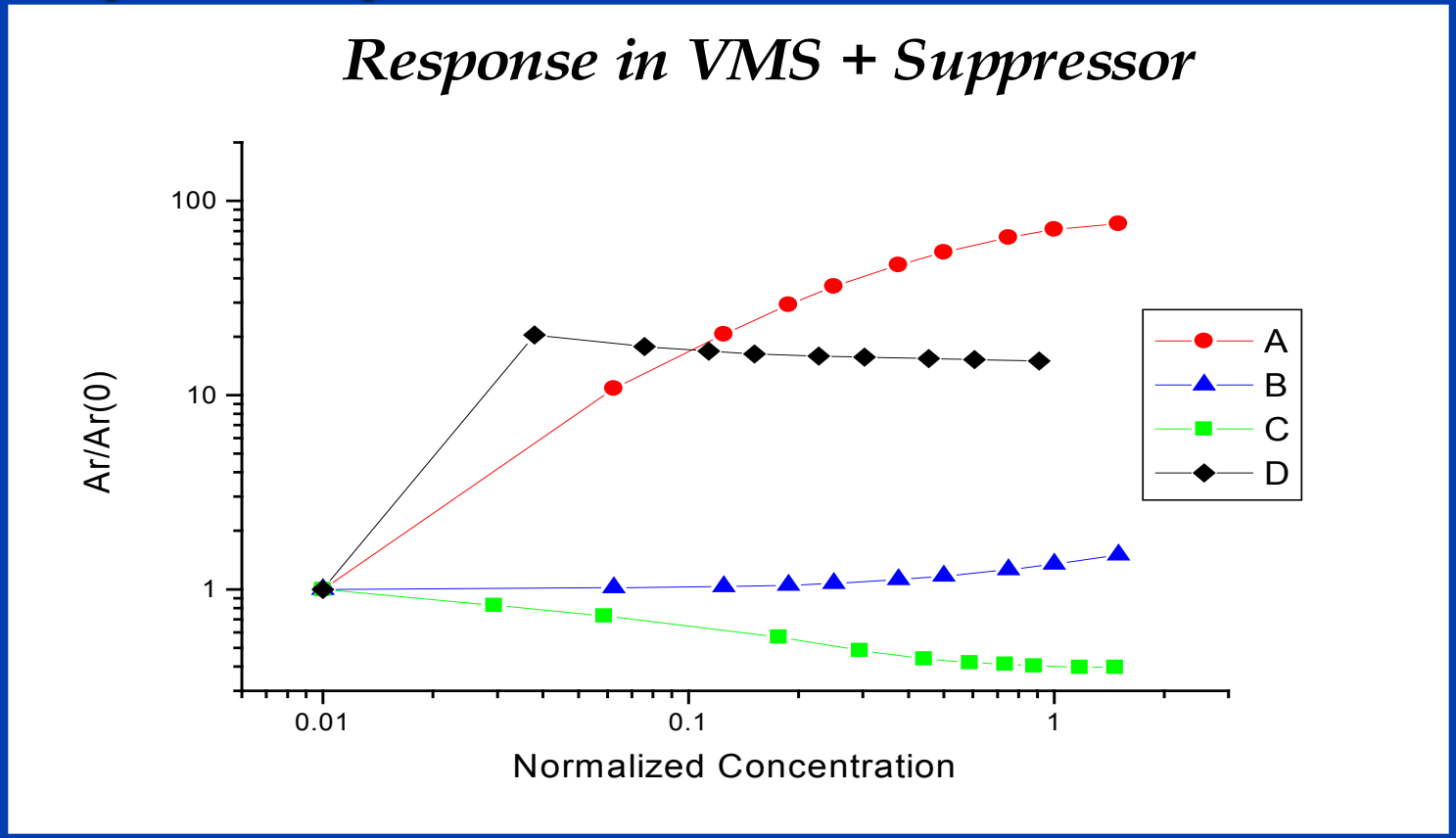


Electrochemical activity (CVS) of Cu EP Additives



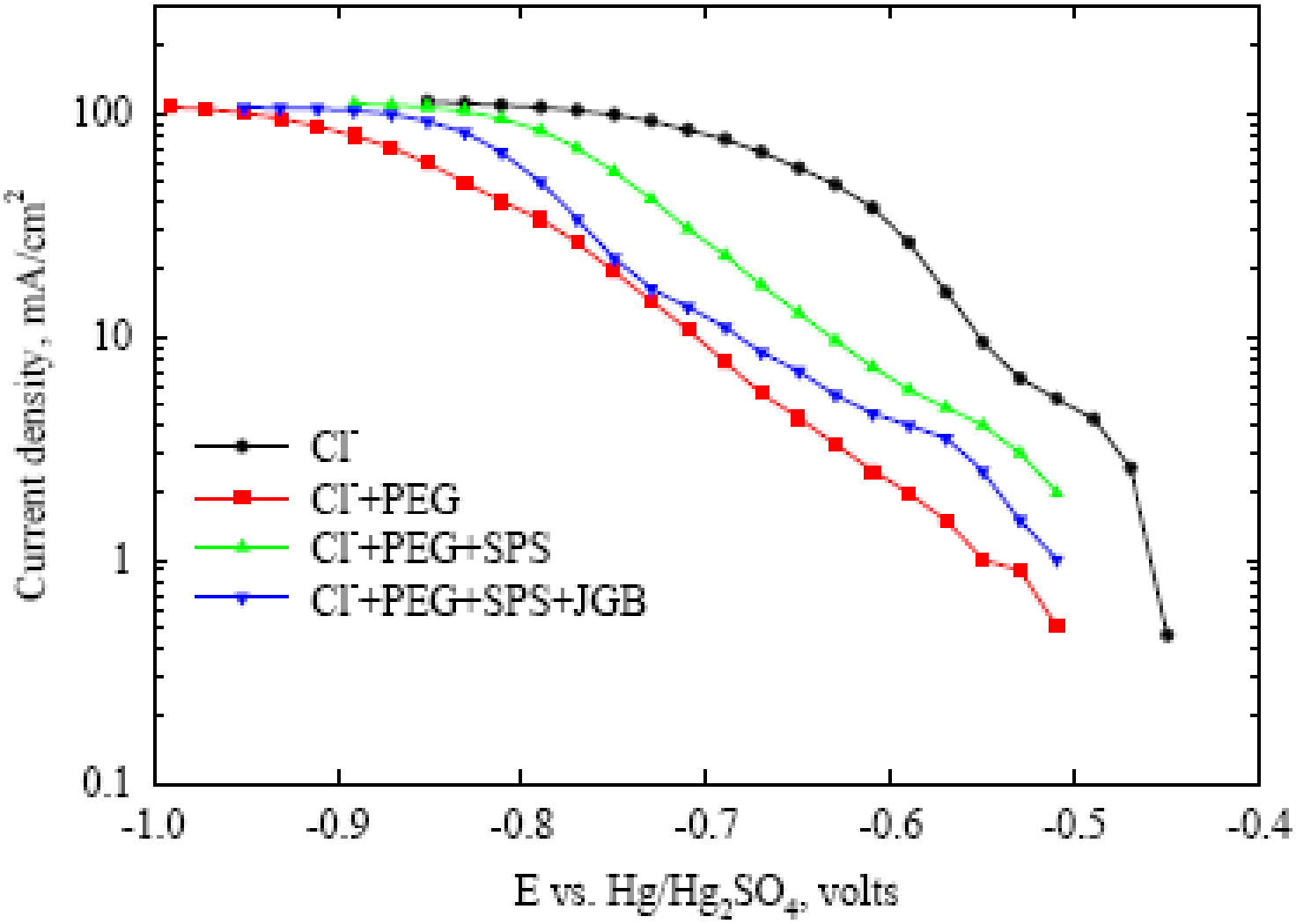
A - Brightner (ASUPP), B - SUPP (wetting agent), C – Leveler (LEV)

Electrochemical activity (CVS) of Cu EP Additives

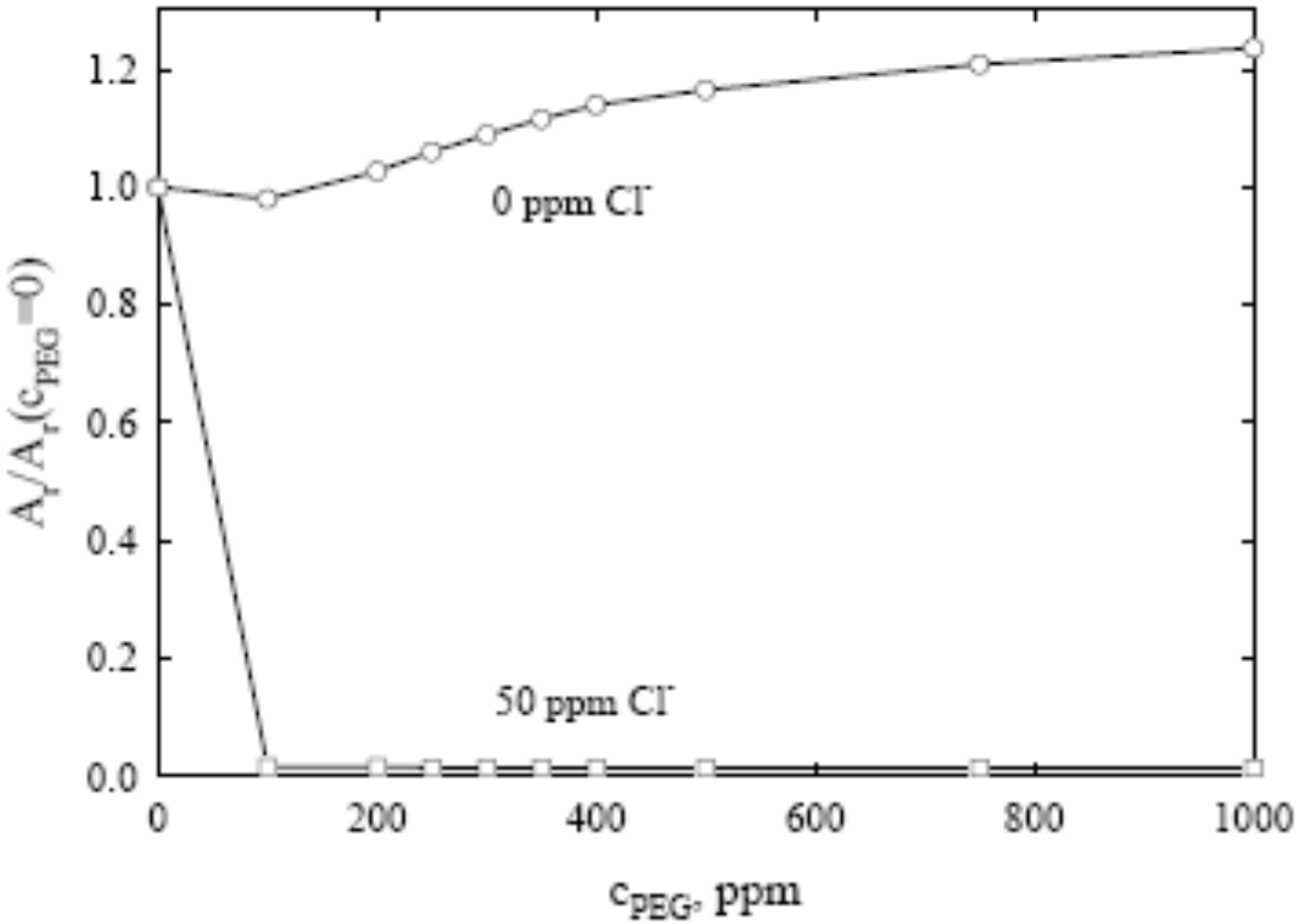


A - Brightner (ASUPP), B - SUPP (wetting agent), C – Leveler (LEV)

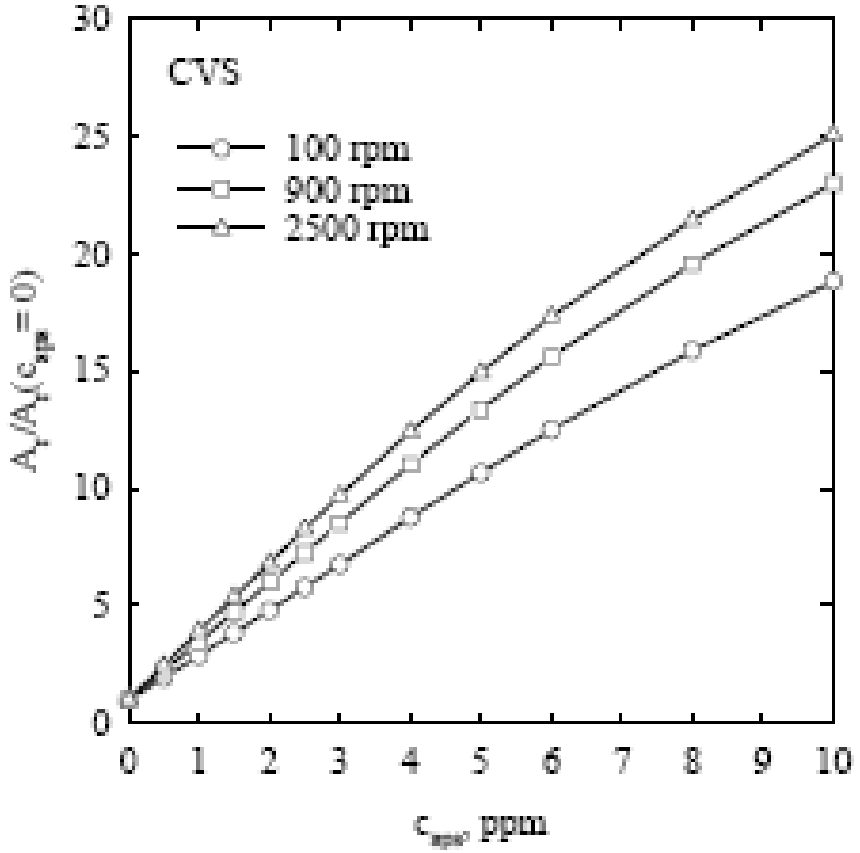
Linear Sweep Voltammetry (LSV)

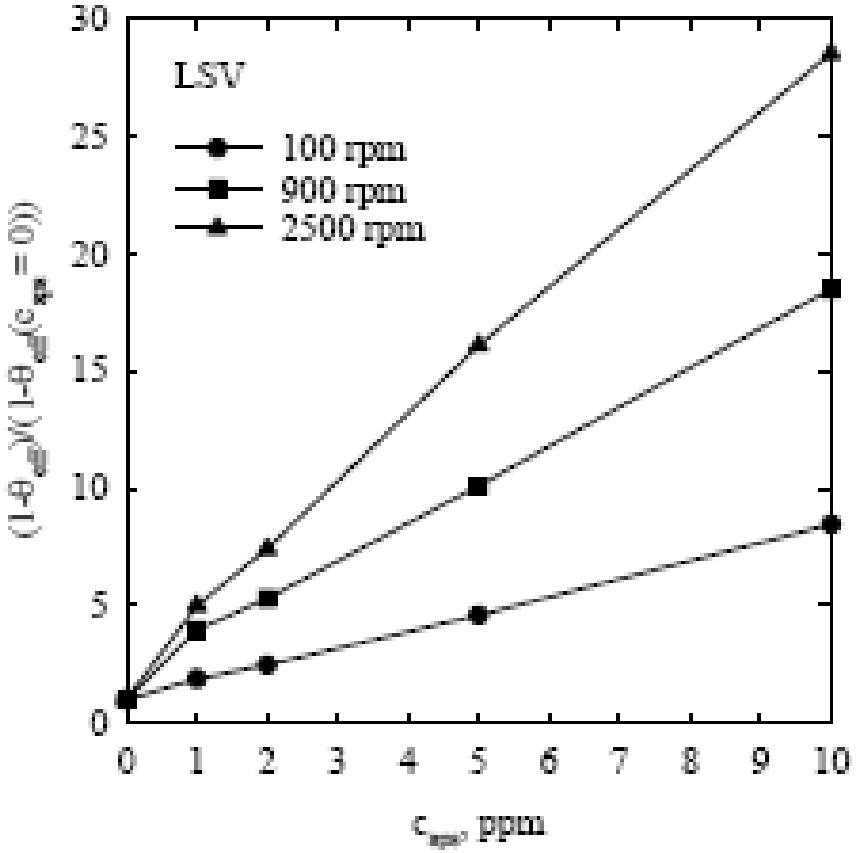


Effect of Chloride on PEG adsorption

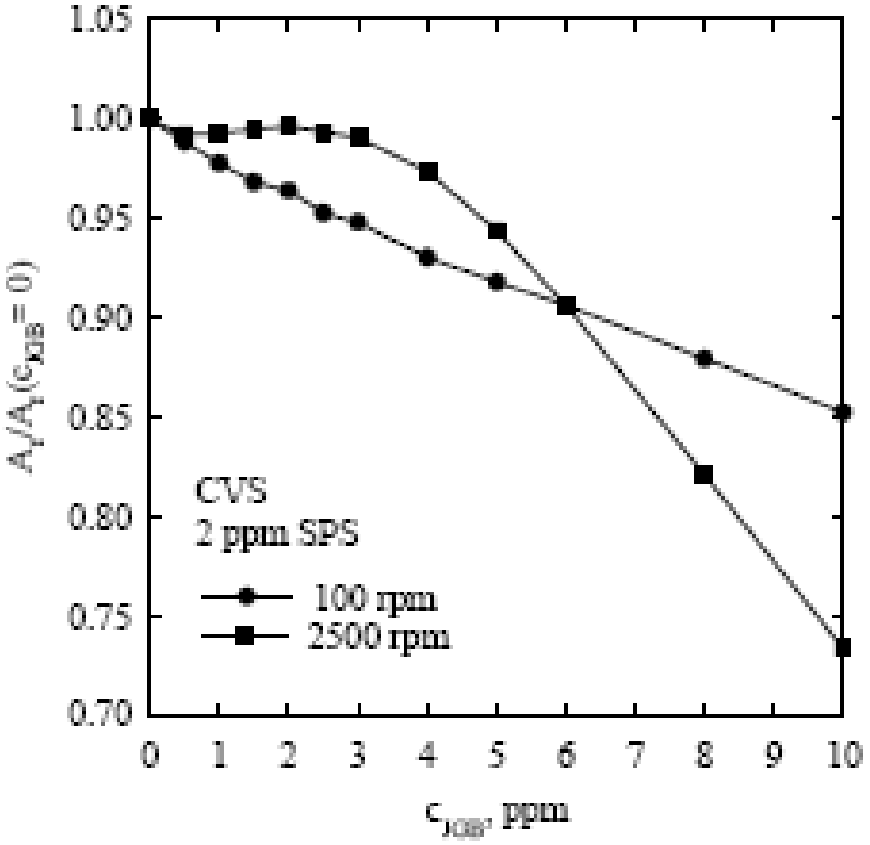


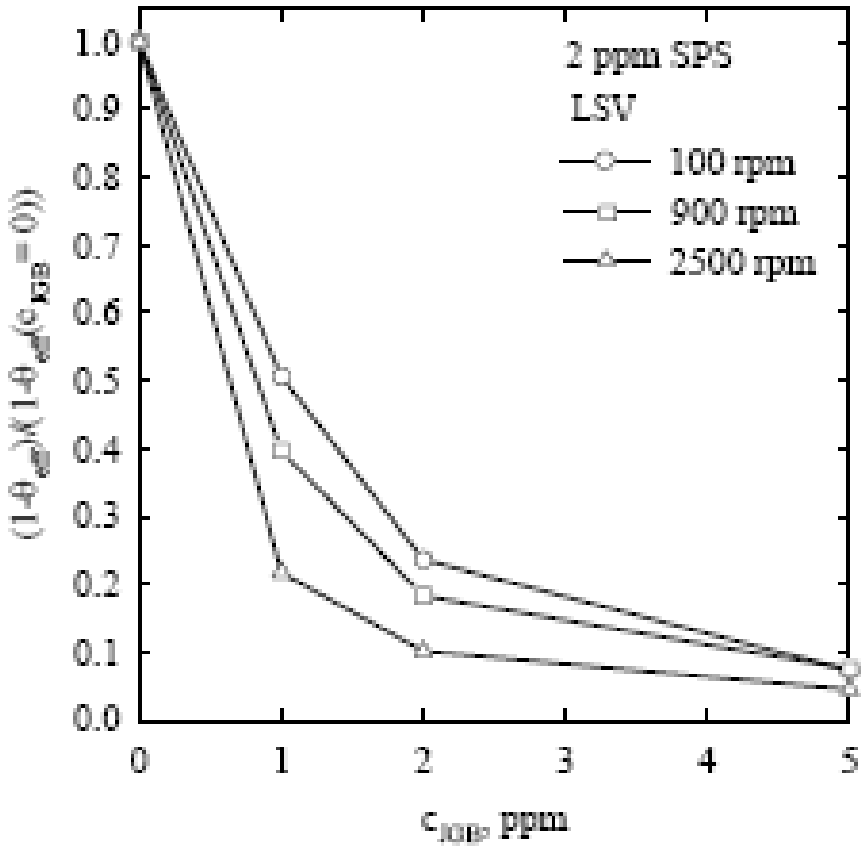
Acceleration Effect of SPS on Cu Deposition

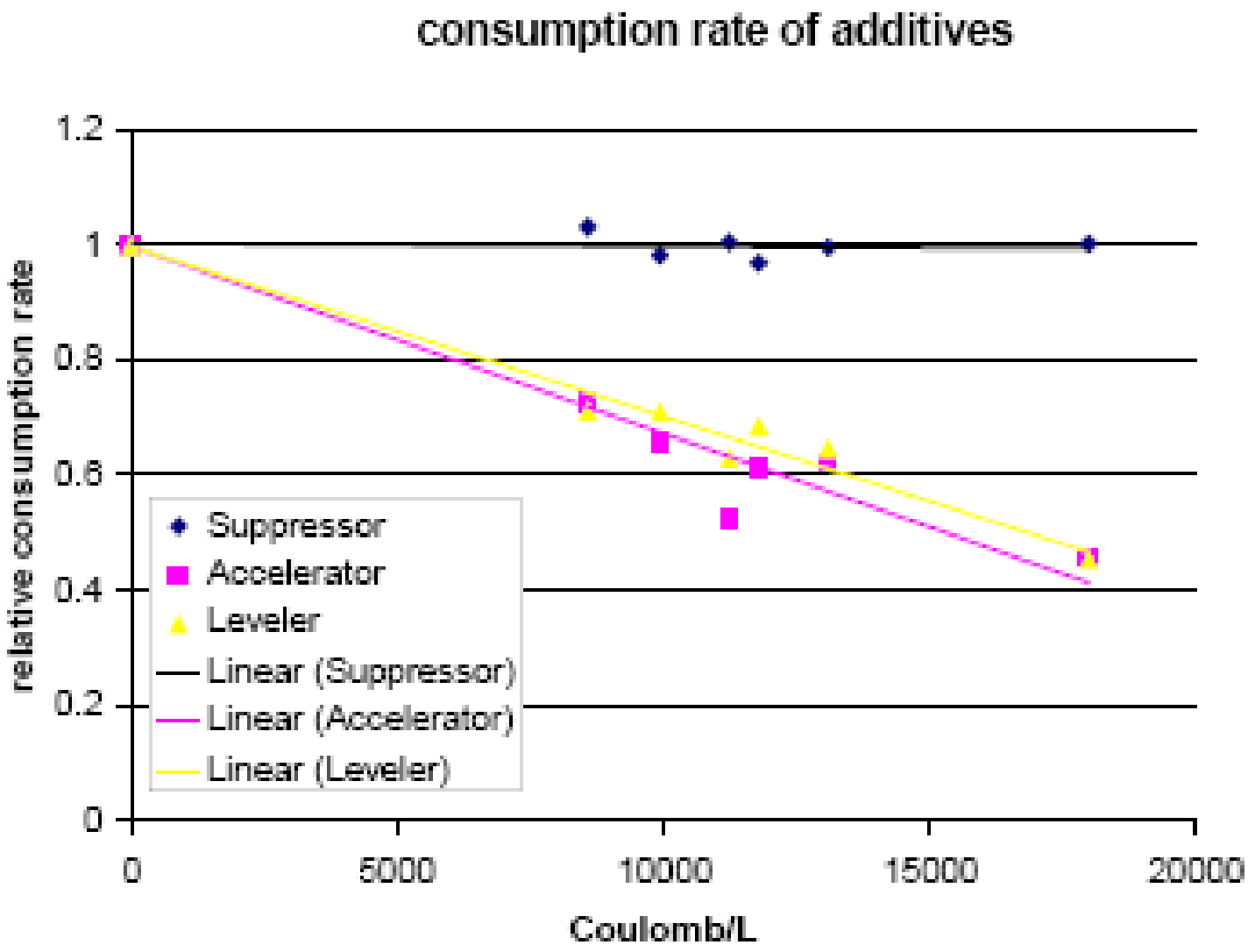




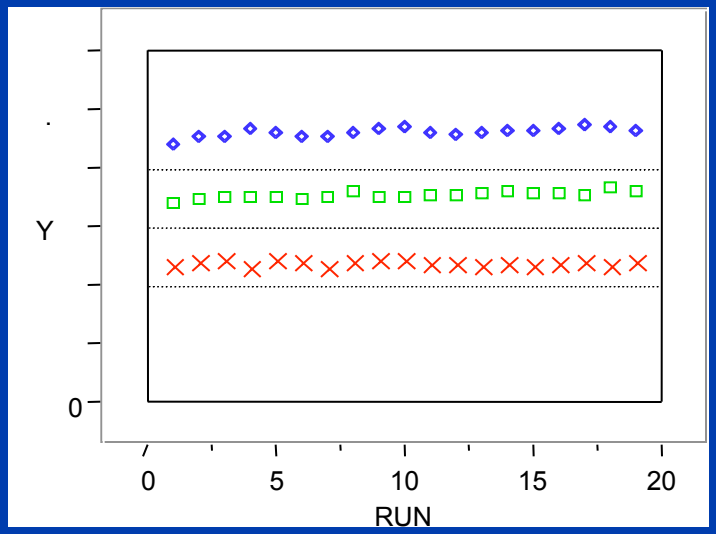
Inhibition Effect of JGB on Cu Deposition

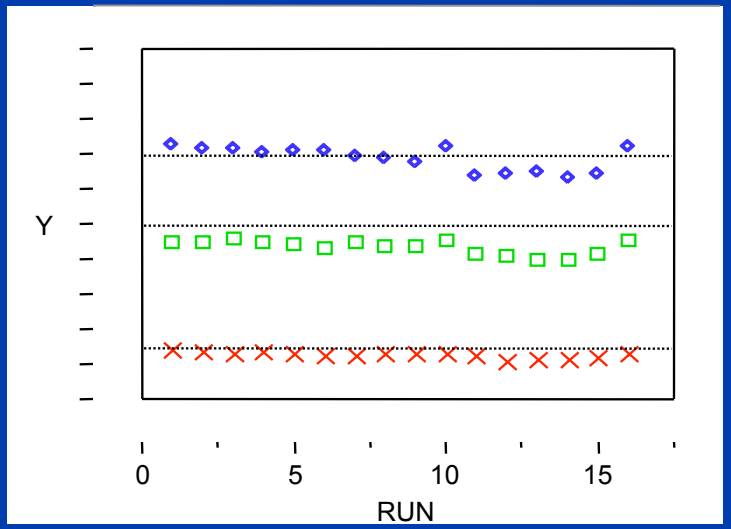





consumption rate of additives
relative consumption rate
1.2
1
0.8
0.6
0.4
0.2
0
0
5000
10000
15000
20000
Coulomb/L
Suppressor
Accelerator
Leveler
Linear (Suppressor)
Linear (Accelerator)
Linear (Leveler)

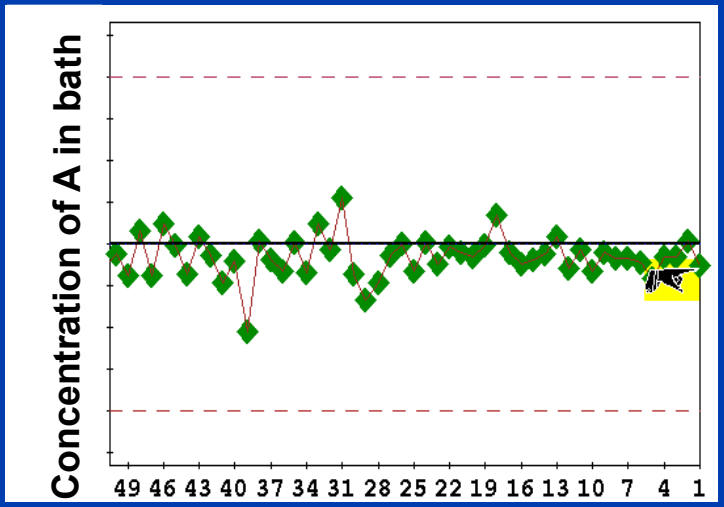
On-line bath metrology/replenishment

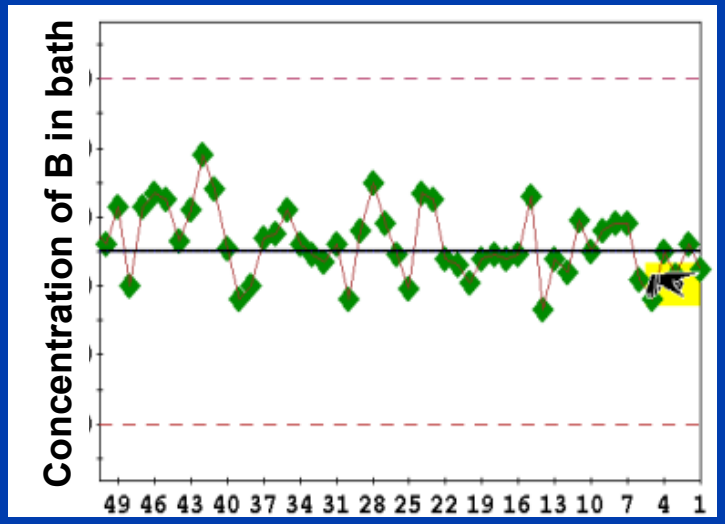




Component A (p/t <0.3)

Component B (p/t <0.3)





Cu Film Properties - Cont

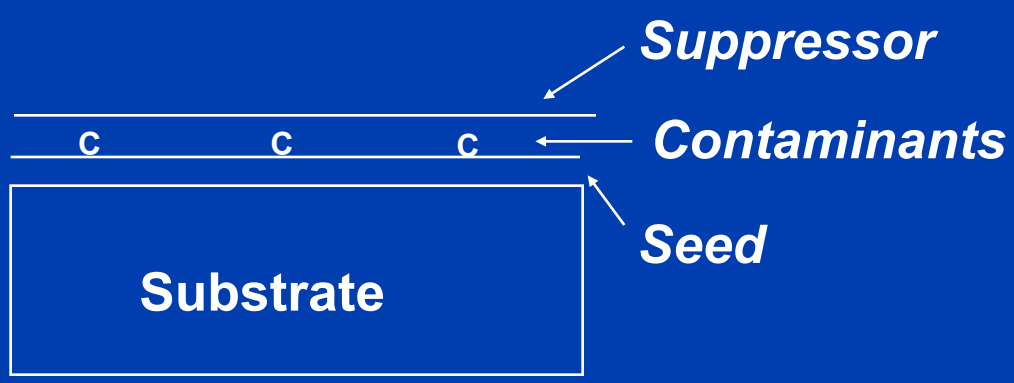
- Ea for PVD CuPd(0.5%) - 1.01 eV, CuPd(1%) - 1.26 eV, for PVD CuSn(0.5%) - 0.95eV, CuSn(0.5%) -1.25eV; Ea for grain boundary diffusion in PVD Cu is 0.8-0.92 eV ([11] D. Gupta, MRS proceed., **337**, 1994, [22] K.L. Lee, C.-K. Hu et al. Appl. Phys., **78**, (1995) 4428)
- PVD Cu (111) crystallographic orientation is enhanced on on TiN film with strong TiN (111) orientation. Superior EM performance was observed in Cu with a strong (111) orientation (about one order of magnitude longer MTTF than that for Cu with random texture) ([12] K.Abe et al. "Cu metal line crystallographic texture control and its electromigration performance as damascene interconnects", VLSI symp, 1997)
- Cu line exhibiting an overall stronge (111) texture showed better resistance to stress-induced void formation in Ta-encapsulated Cu interconnects ([13] J.A. Nucci et al., Appl. Phys. Lett., **69** (26), 1996, 4017)

Cu Film Properties

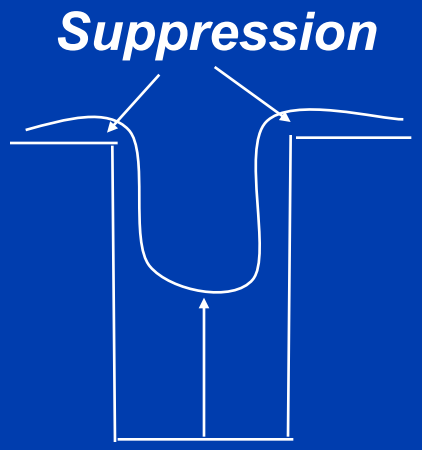
- Annealed electroplated Cu film deposited on PVD Ta/Cu exhibit strong (111) texture (4% random, tilting angle 2.57); plated lines formed in sub-micron trecnhes also exhibit strong (111) texture (about 5-9% random, tilting angle about 2-4)
  ([14] V.M. Dubin et al. "Microstructure and mechanical properties of electroplated Cu films for damascene ULSI metallization". 1997 Fall MRS meeting)
- Plated Cu grains in trenches are quite large. One or two grains fill the entire trench (due to secondary grain growth driving by stress release); Plated Cu: mean grain - 1.1 um, sigma - 0.45 [14]
- The agglomeration of Cu appears when the wetting characteristics of barrier is poor. The wetting characteristics of barrier layer for Cu is in the following order APT(Ar plasma treated)-TiN>APT TiW>TiW>>TiN; the intensity of Cu (111) peak is in the following order: APT TiN>TiN>TiW>APT-TiW
  ([15] S. Hirao et al. 1997 VLSI Symp.)

MB/ Cu void defects

- Cu voids (pin holes) defects due to MB and gap fill issues have been reduced/eliminated by using CuEP chemistry which provide
  - uniform Cu nucleation due to high suppression and low sensitivity to b/s surface contaminants
  - superior gap fill due to higher concentration of ASUPP and stronger suppressors being used



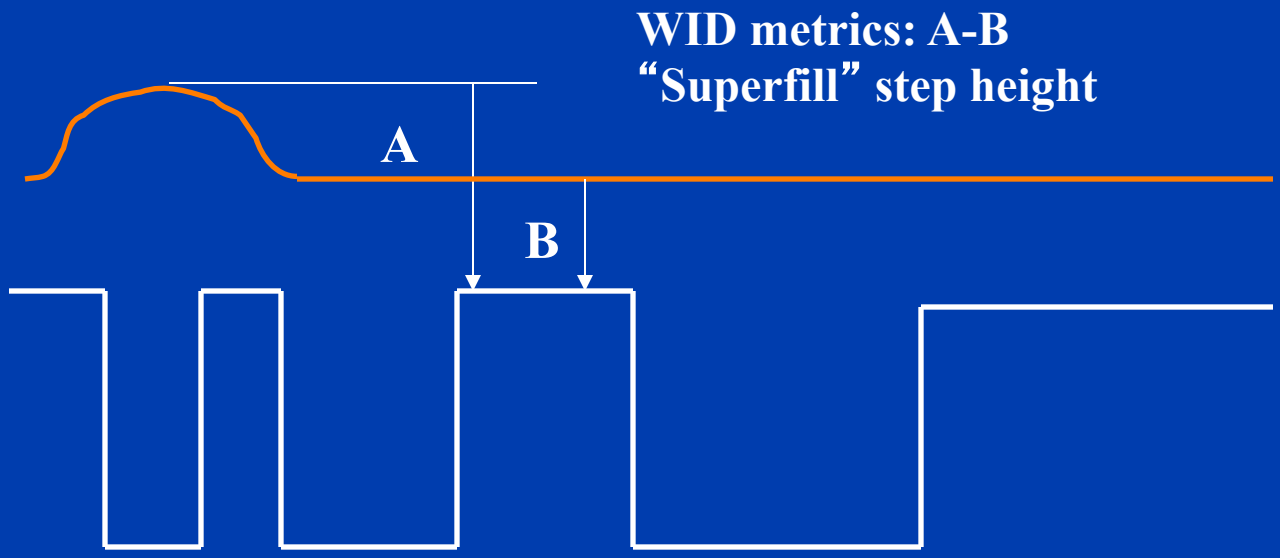
Suppression of contaminants



Acceleration

Uniformity

- Within Wafer Non-Uniformity (WIWNU) - about 2%, 1 Sigma
- Within Die Non-Uniformity (WIDNU) - step height over dense features (<1000A)



Uniformity – Role of Additives

Cl^-, PEG, SPS

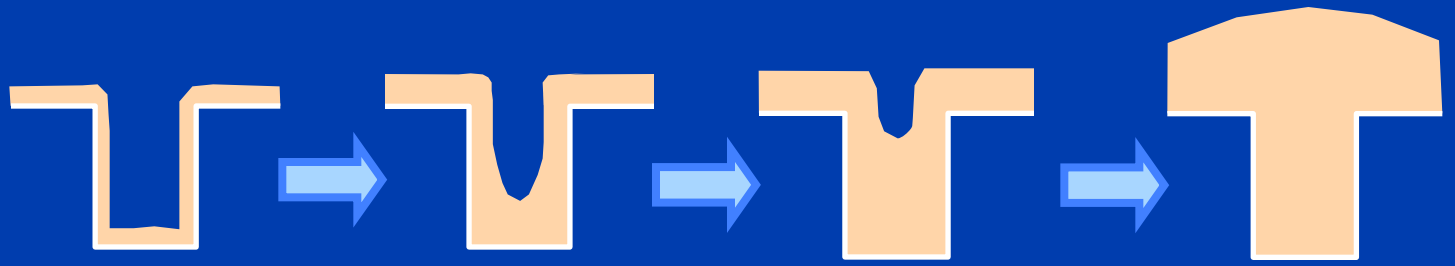
"Bottom-up growth" and **"Overfill phenomenon"**

Preferential Cu growth upward from the bottom

- Superfilling

Formation of Cu bumps above Cu-filled trenches

- Disadvantageous for CMP

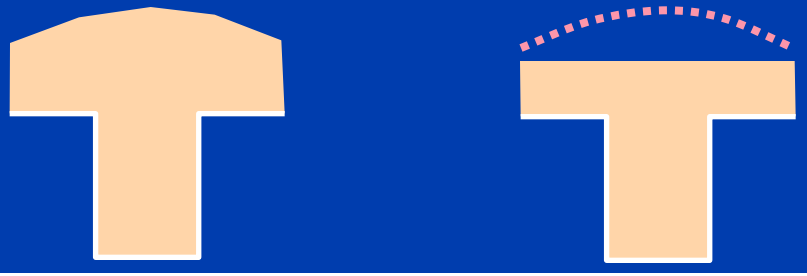


Bottom-up growth **Overfill phenomenon**

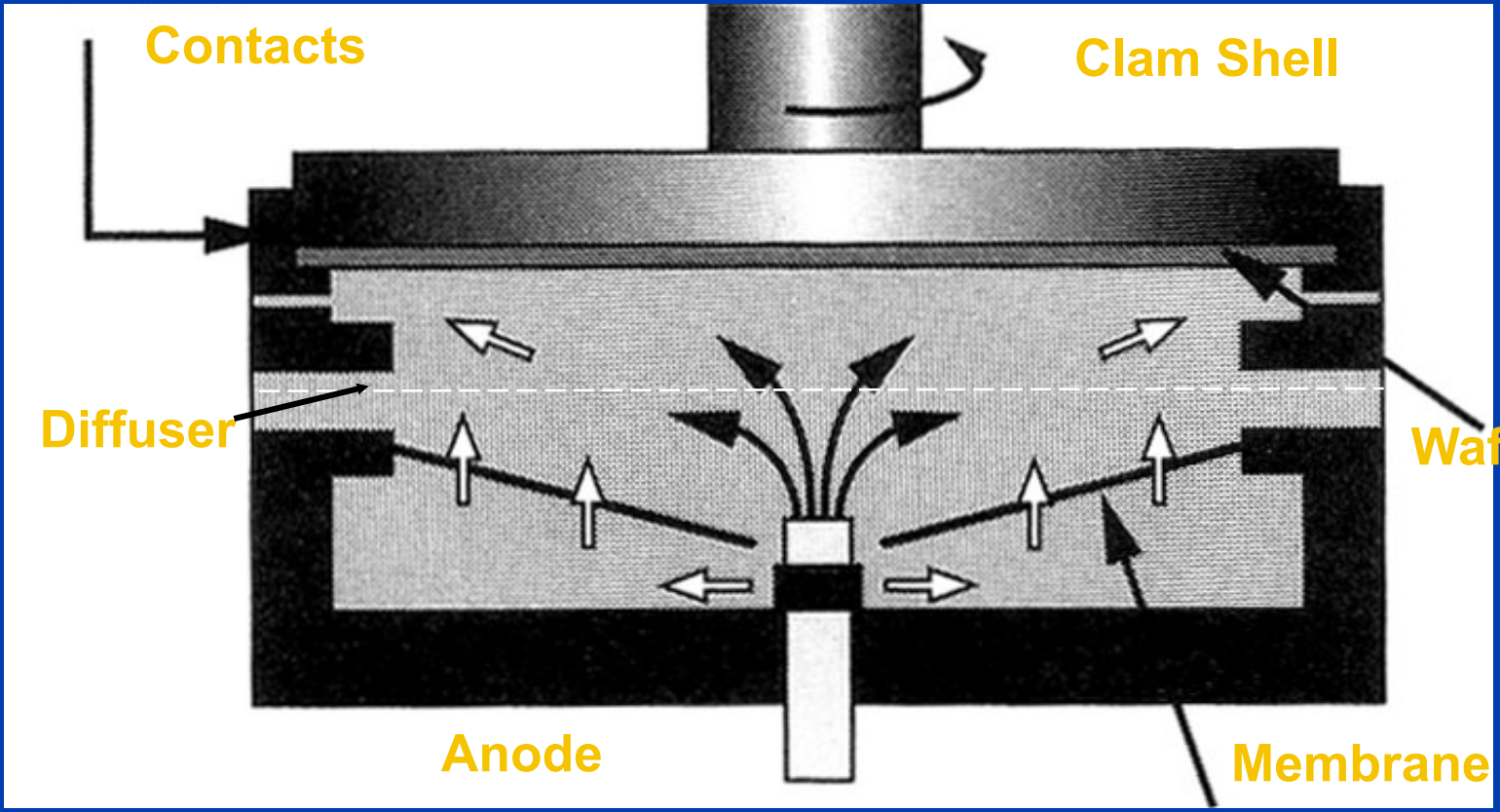
JGB

Suppression of "overfill phenomenon"

Without JGB **With JGB**

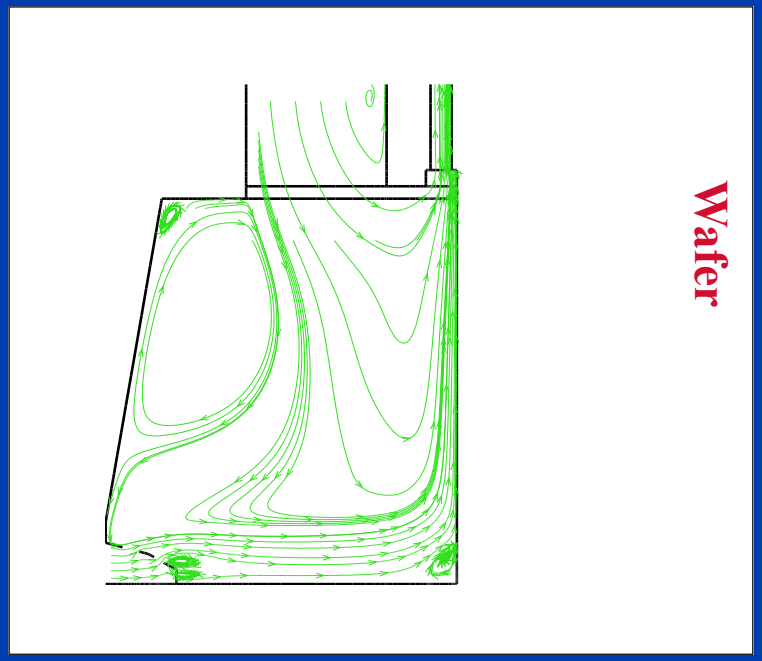


Plating cell

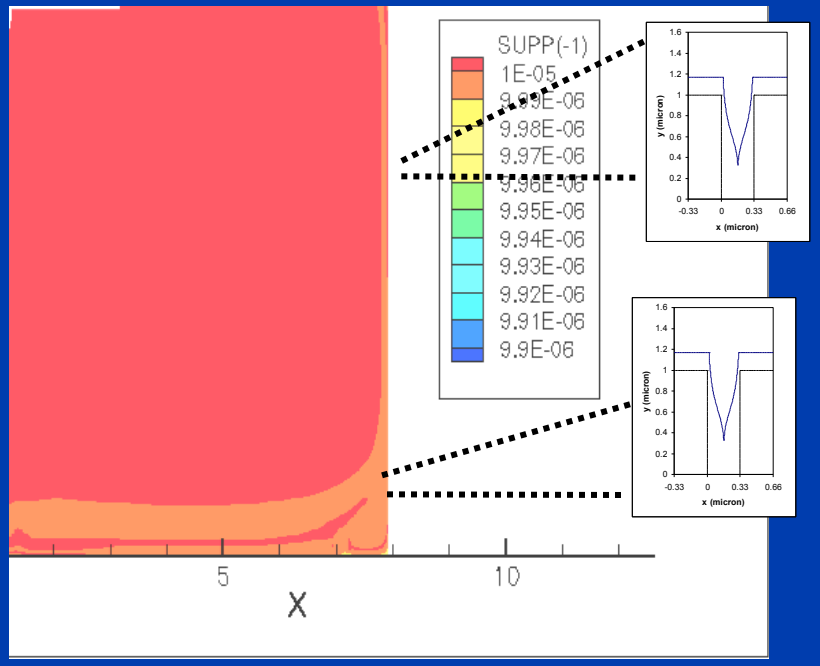


Integrated Electroplating Modeling

Fluid flow simulation

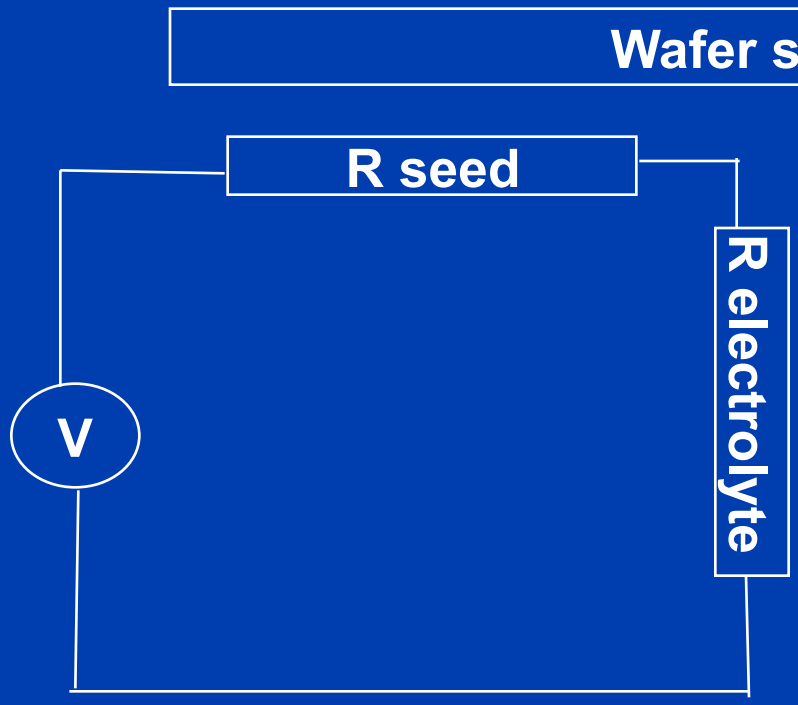


Additive Concentration Profile



- **Wafer-scale tertiary current distribution model, based on finite-element method (FEM), was used to optimize flow field and concentration variations**

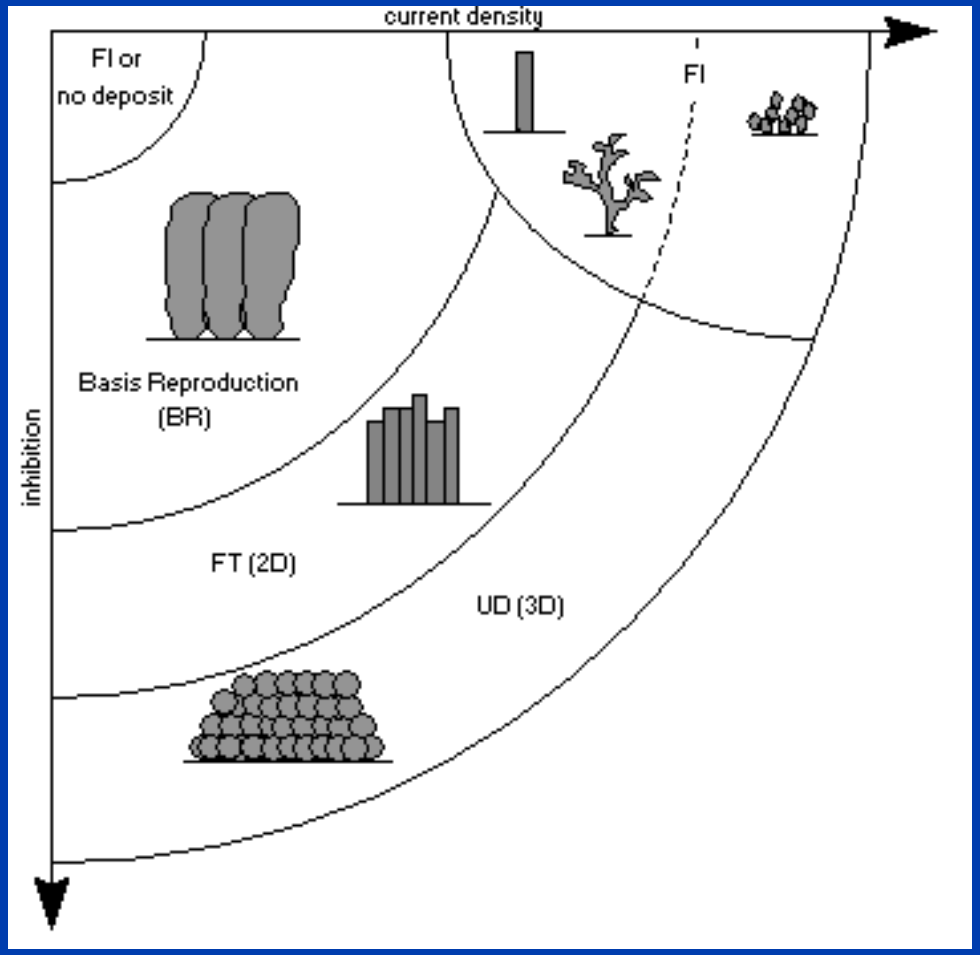
Terminal Effect



I = V/(R seed + R electrolyte)

High R electrolyte (low acid) will dominate and mitigate increase in R seed due to thin seed (i.e. provide low WIWNU)

Cu Film Microstructure vs Dep. Conditions



FI	Field Oriented Crystals
BR	Basis Reproduction
FT	Field Oriented Texture (2D nucleation)
UD	Unoriented Dispersion (3D nucleation)

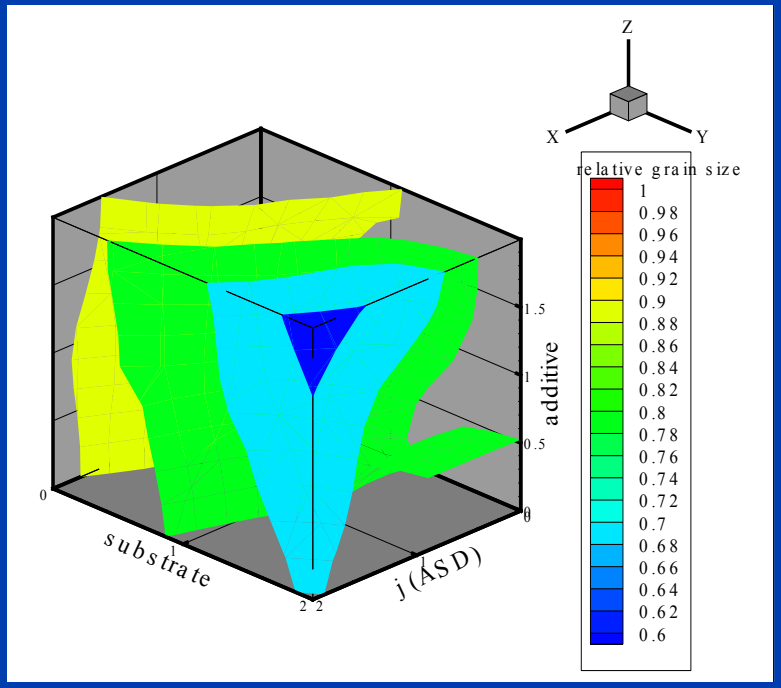
Winand's diagram: high current density study (70s)

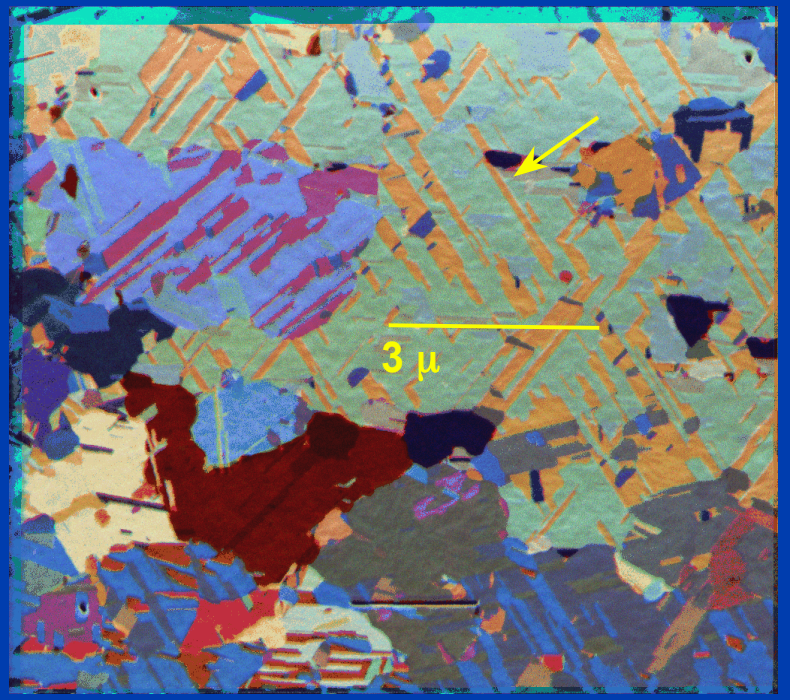
- **Deposit structure as a function of current density and inhibition strength**

Limitations:

- **Inhibition/Additives is not quantified**
- ***Structure classification not clear***
- **Diagram designed for thick films (>30μm)**
- **Impact of substrate missing**

Plated Cu Film Microstructure

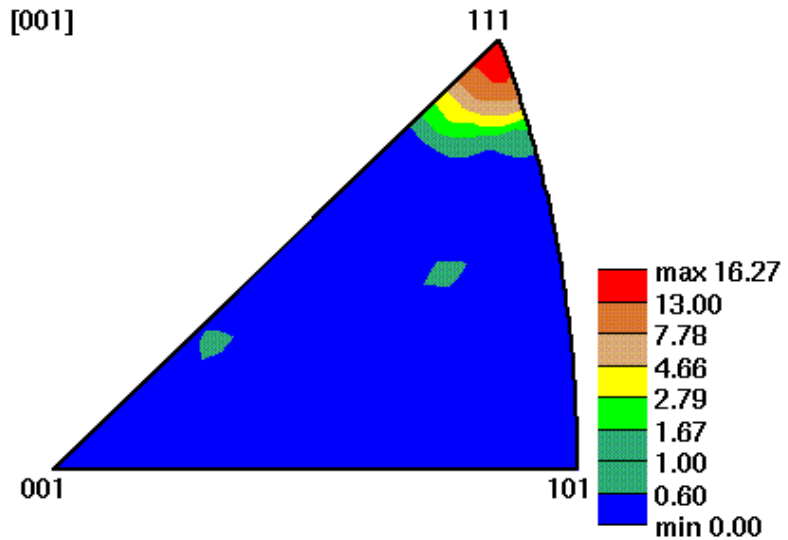


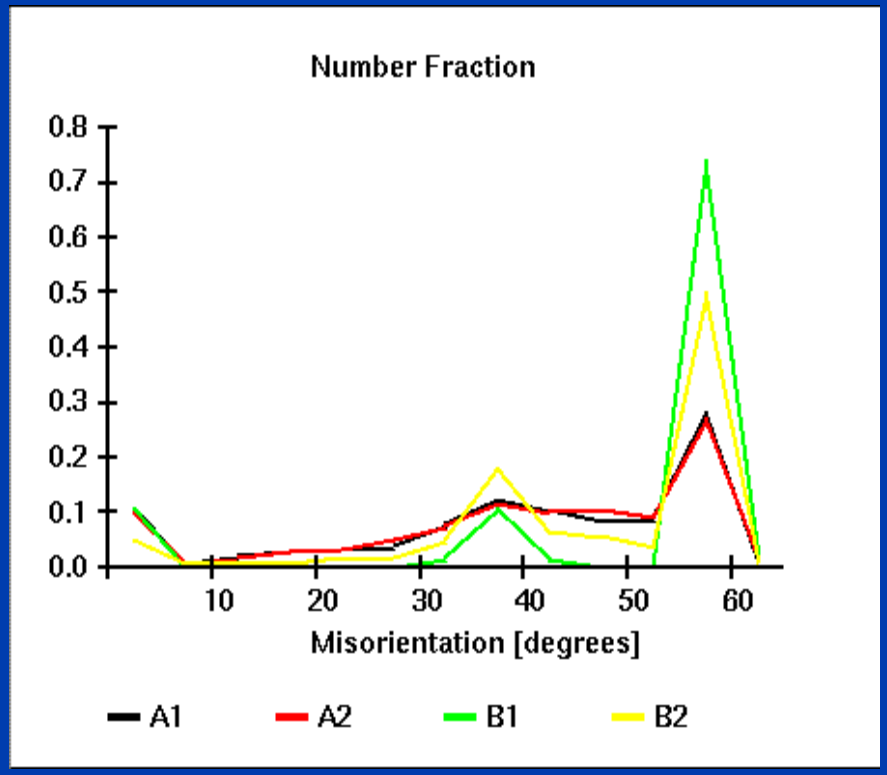


- A new approach based on extension of Winand diagram to 3D was done to investigate grain size distribution
  - More textured substrates lead to more nucleation sites
  - Higher current densities lead to higher nucleation rate
  - Higher additive levels reduce grain growth
  - these effects led to smaller grain sizes

Plated Cu Film Microstructure

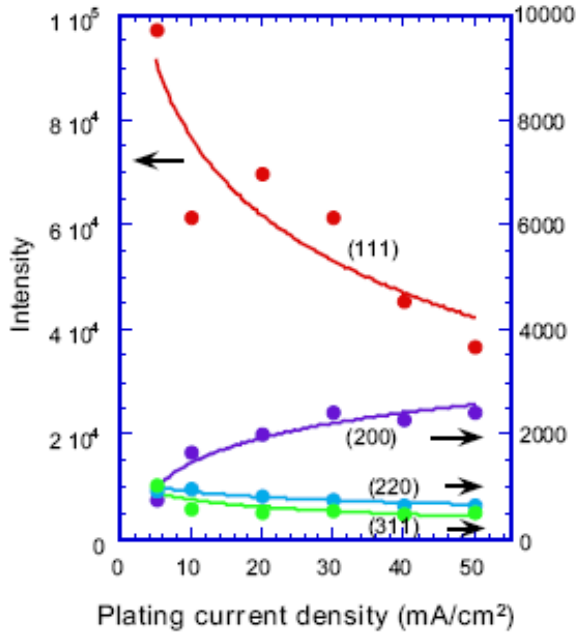
(111) - strong texture
(200), (220) and (311) - small
but measurable components



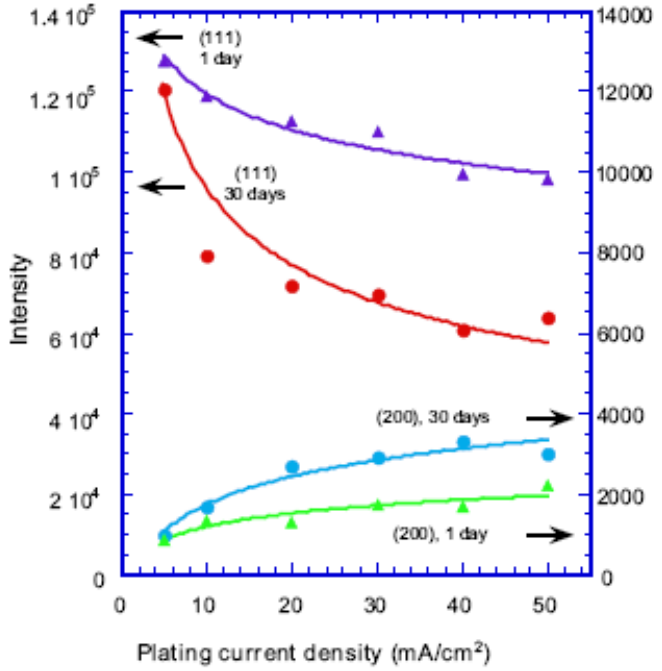


36 and 60 degree mis-orientation grain boundaries correspond to twin grain boundaries in copper

Cu Texture

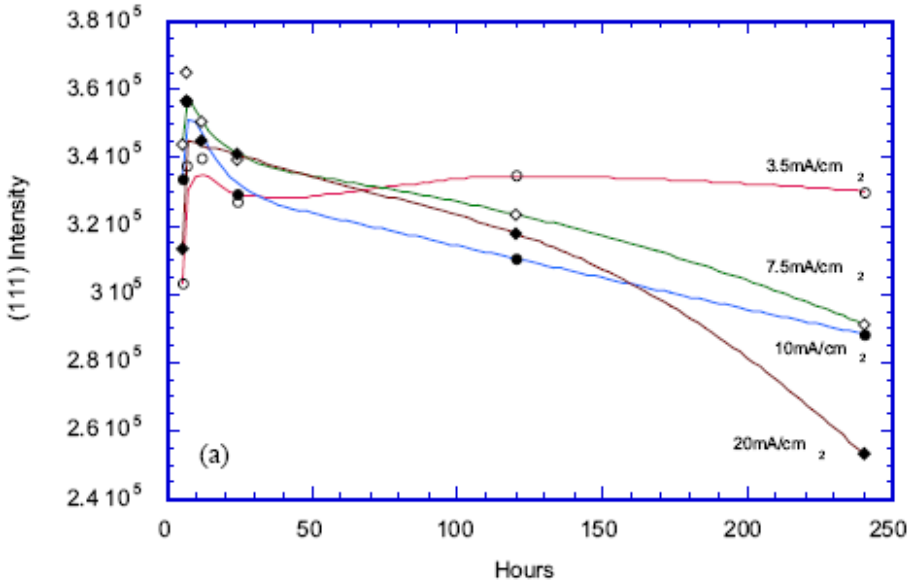


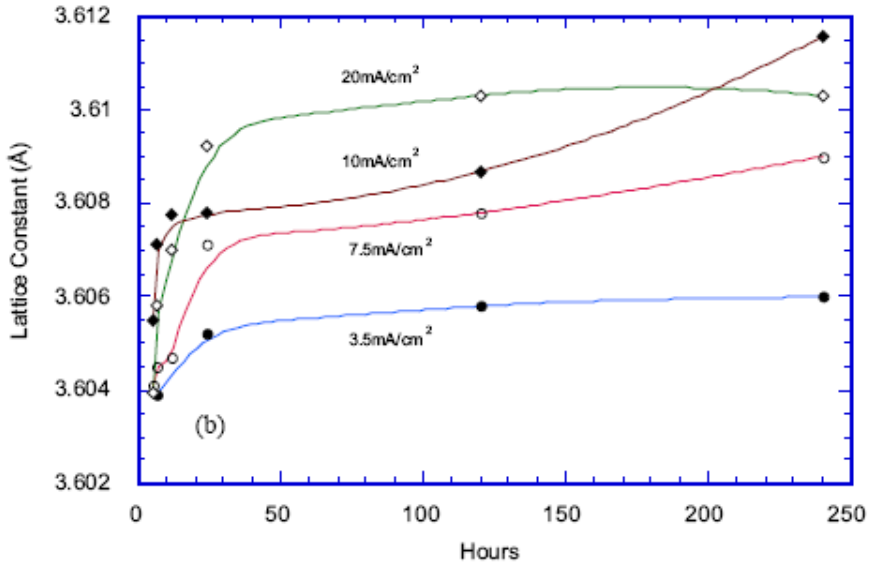
Texture variation with plating current density in films plated without additives. 30 days aged films.



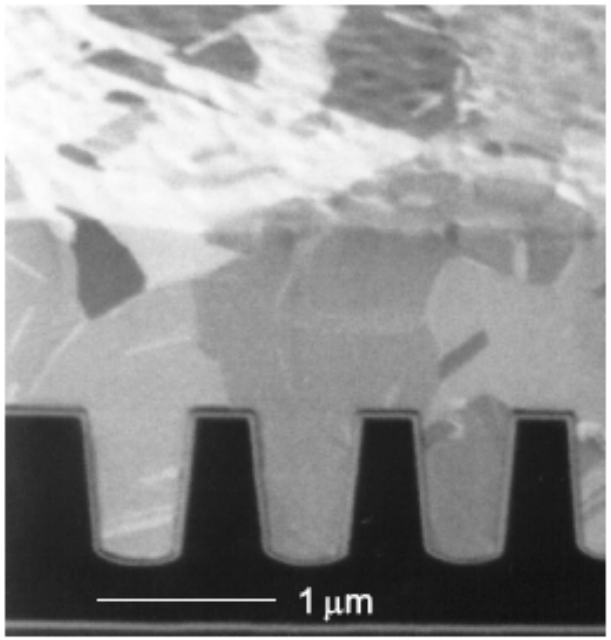
Texture variation with plating current density in films plated with additives.

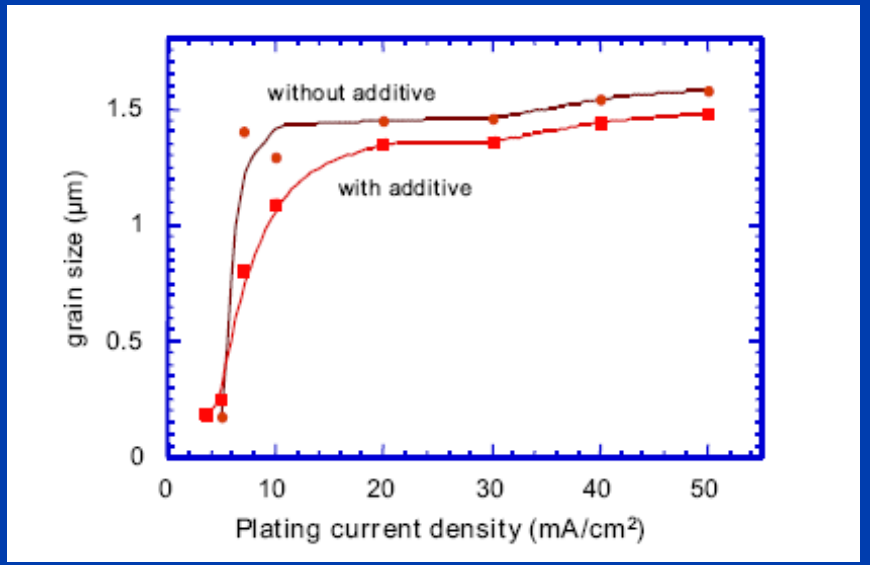
Cu Texture Evolution

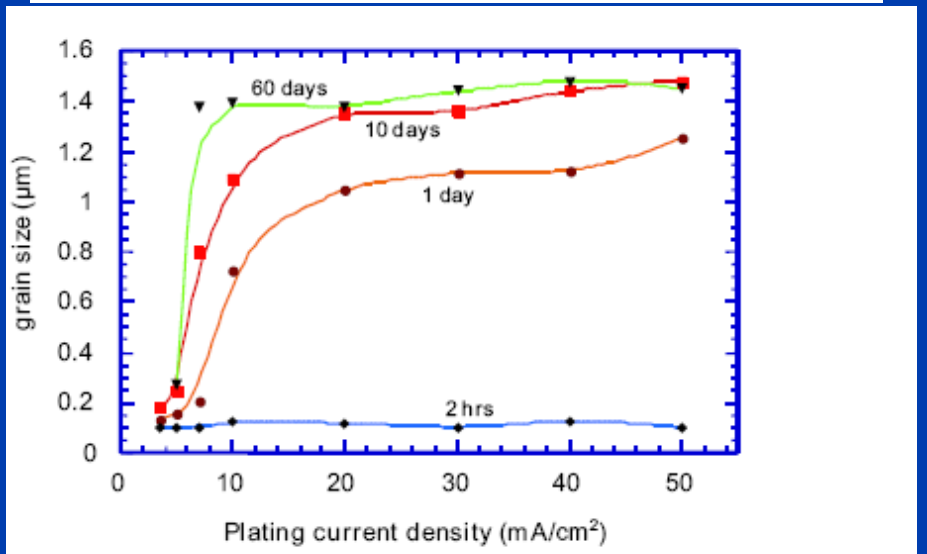




Cu Grain Size

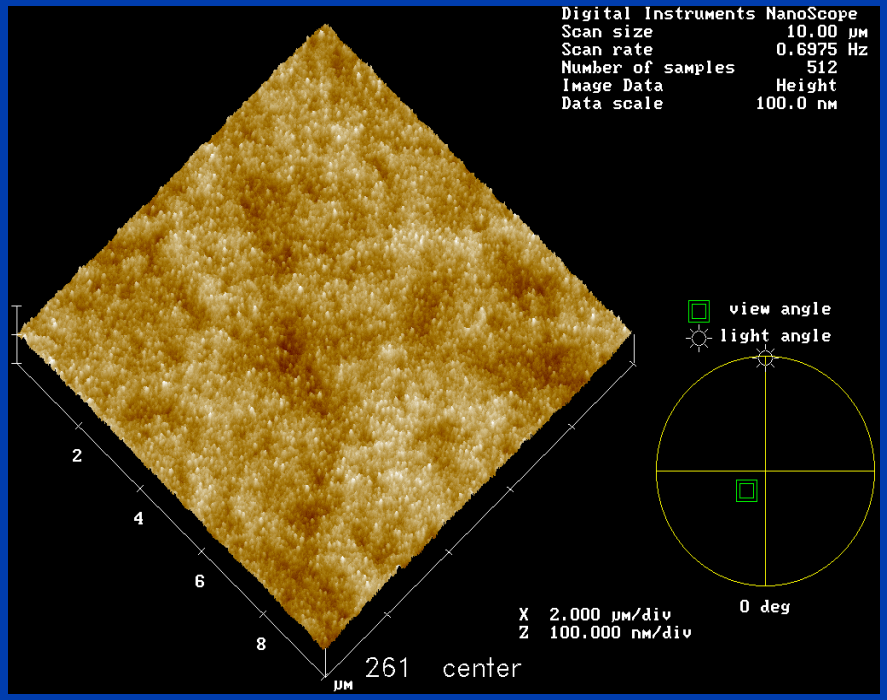


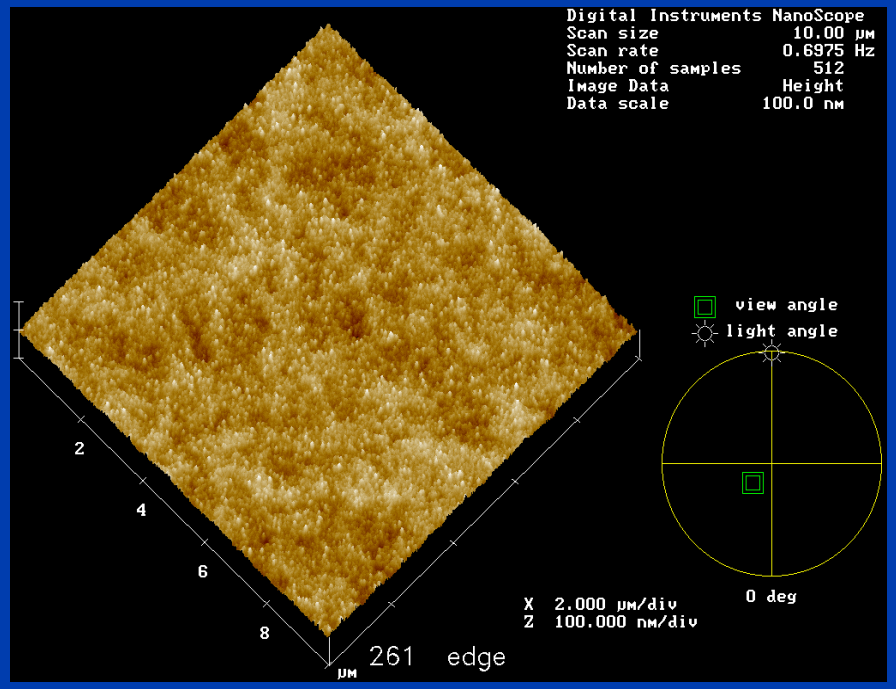




Grain size evolution for Cu films plated at different current densities from electrolytes containing additives.

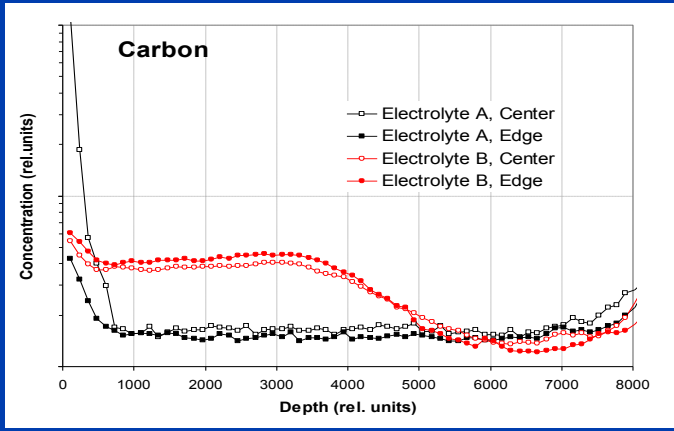
Electroplated Cu surface roughness

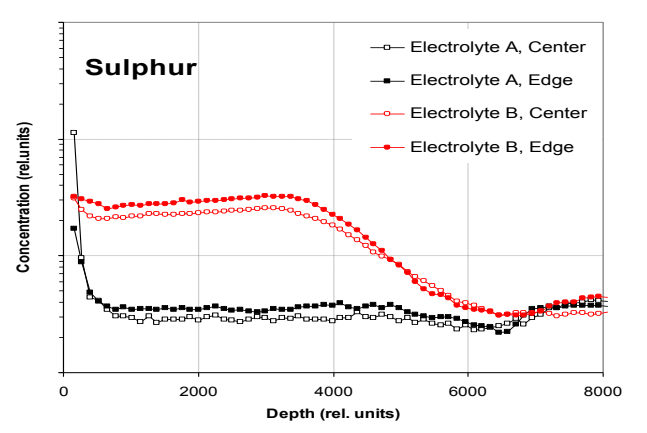


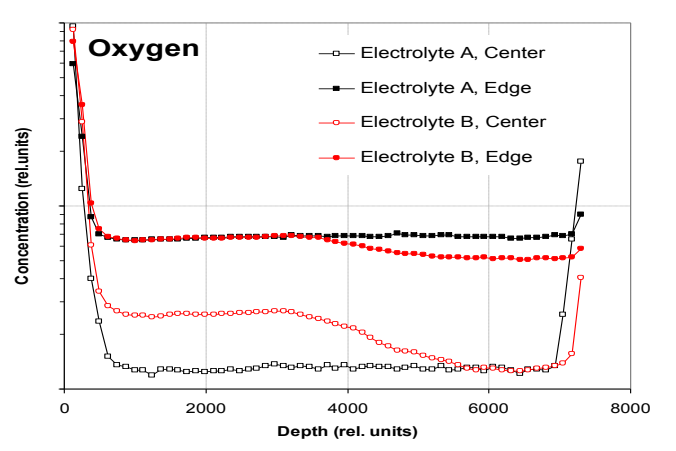


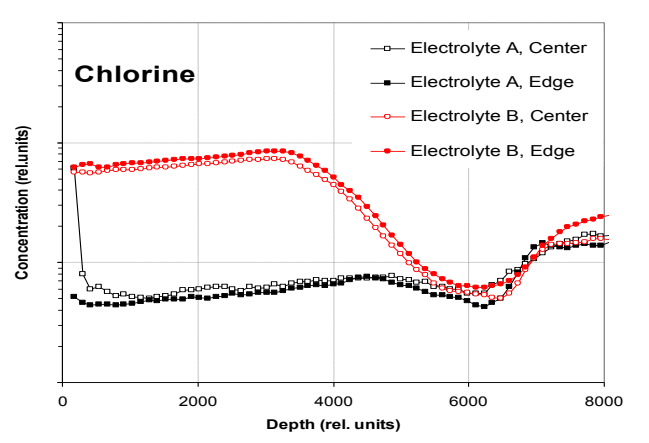
AFM surface roughness is in the range of RMS 5-6 nm (1 μm thick film)

Electroplated Cu Film Composition



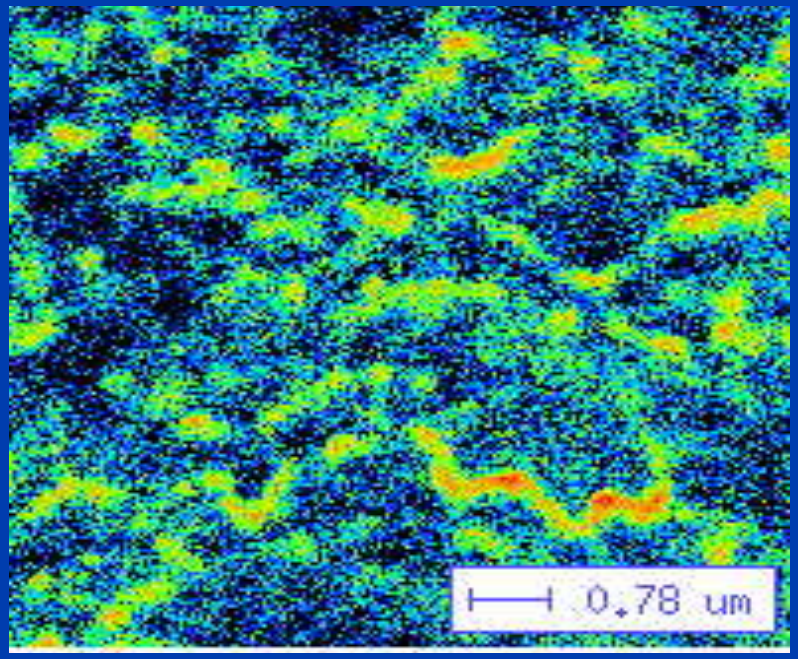


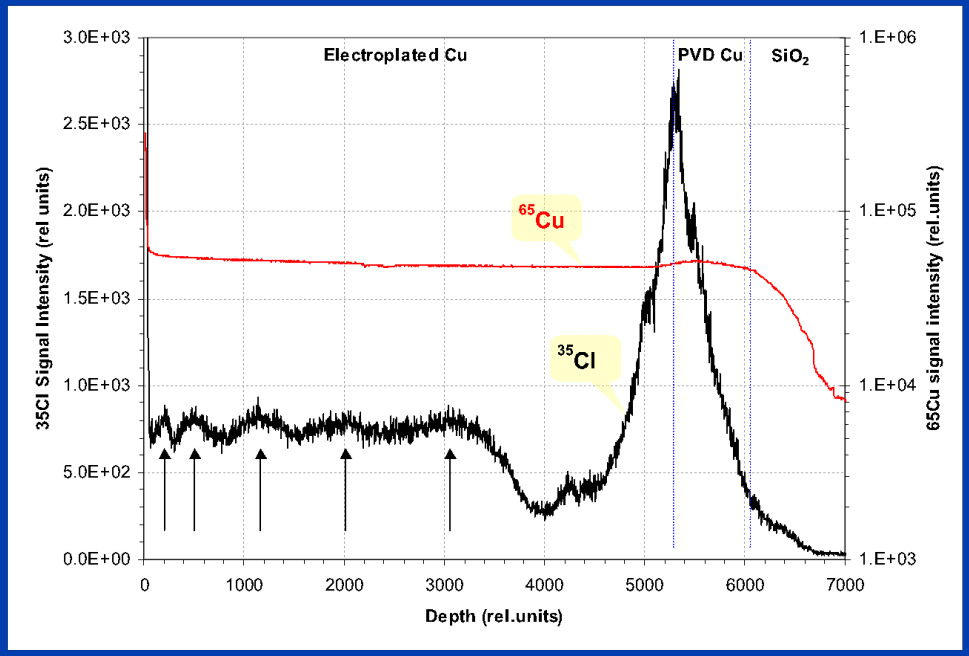




- Incorporation of S is proportional to ASUPP
- C inclusion in the deposits increases w/ TOC level in the bath
- Incorporation of trace impurities in the film depends on the electrolyte being used

Electroplated Cu Film Composition

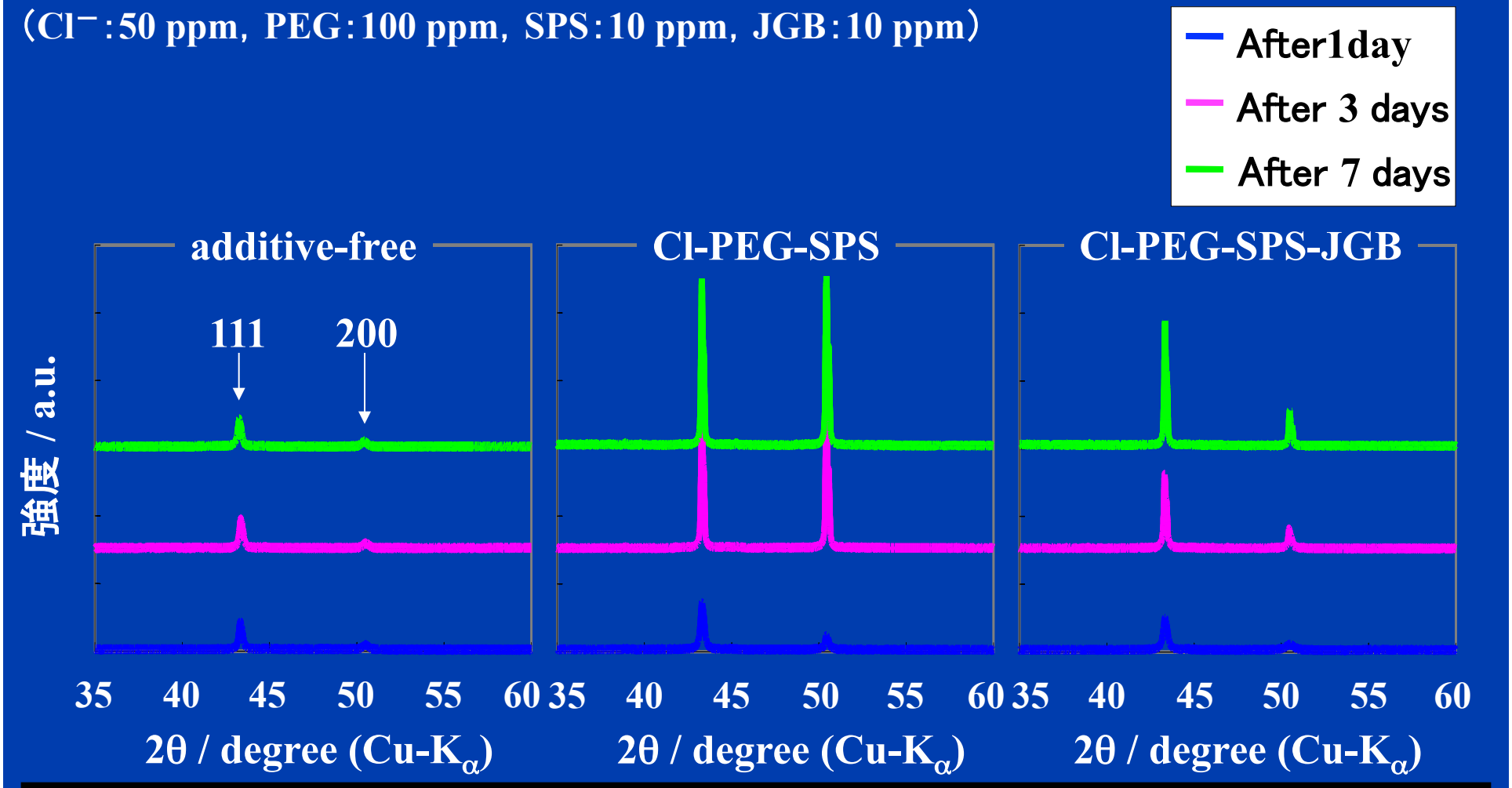




Trace impurities are distributed on the grain boundaries

Variation of Cu Films with Time

（Cl^-：50 ppm，PEG：100 ppm，SPS：10 ppm，JGB：10 ppm）



Cu(111)

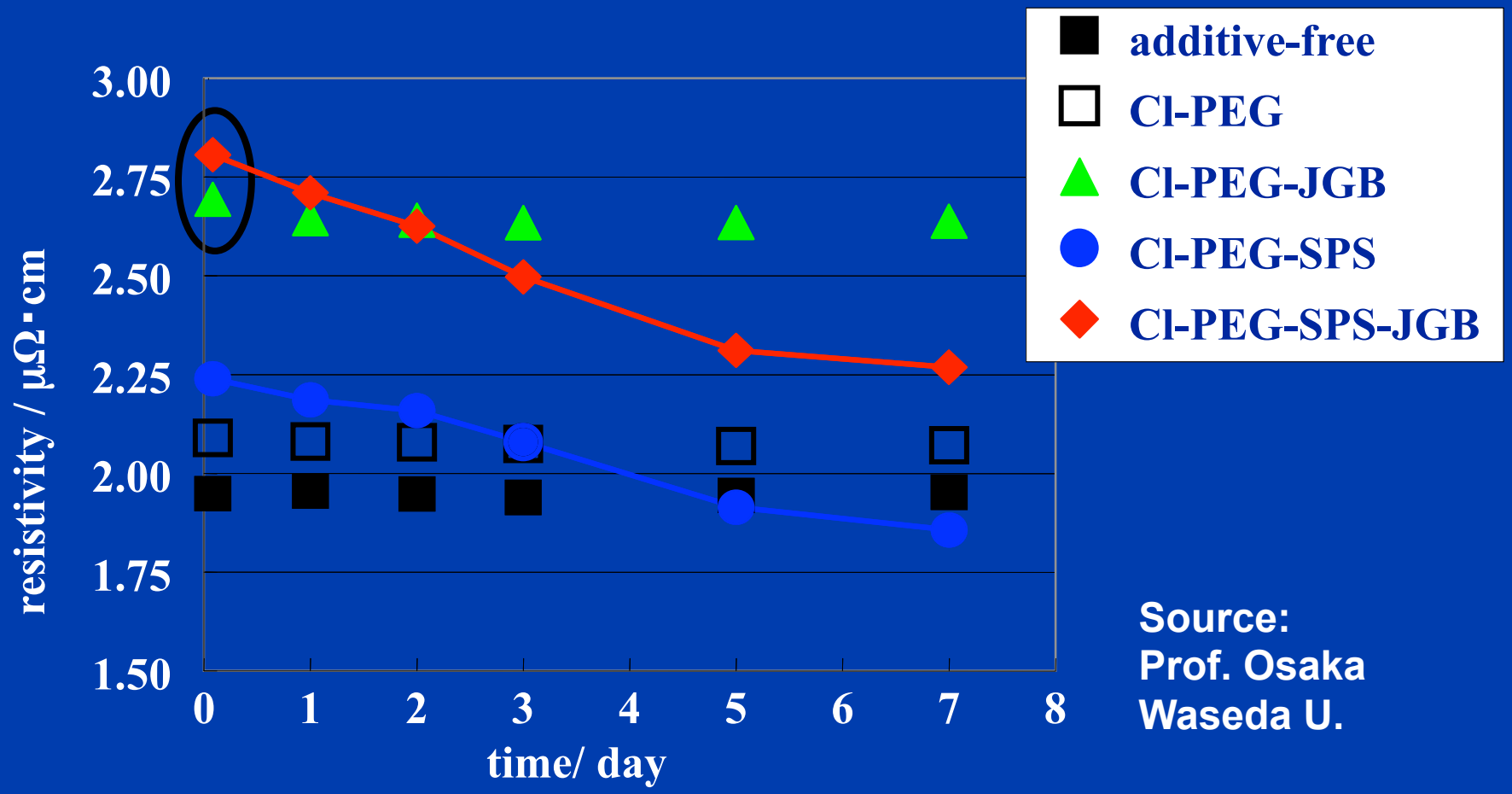
Cu(200)

Self annealing effect

Source:
Prof. Osaka
Waseda U.

Variation of resistivity on time

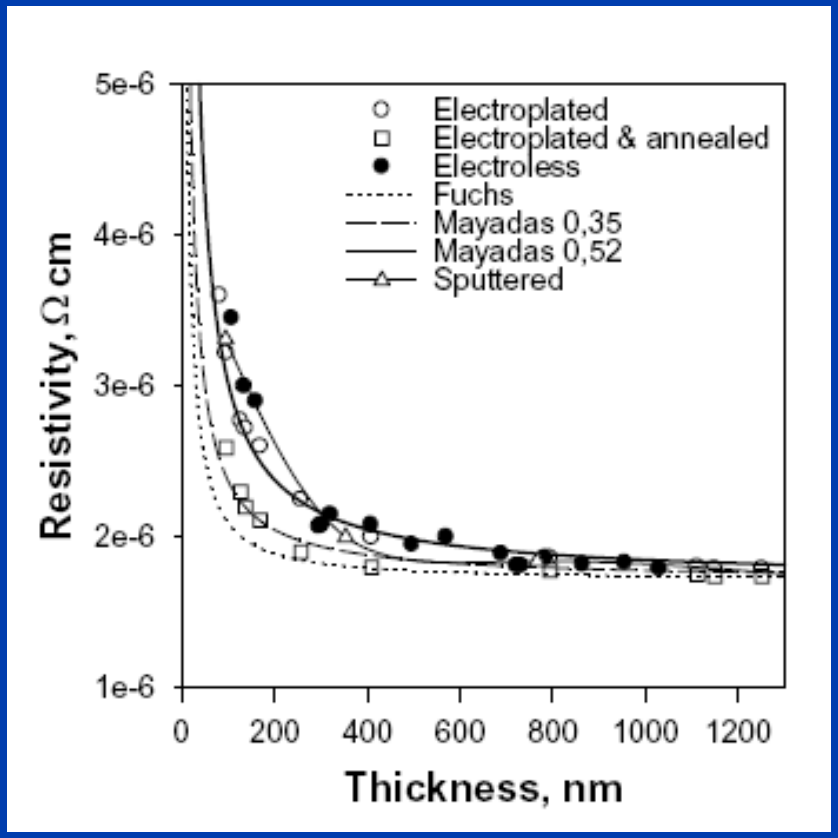
（Cl^-：50 ppm，PEG：100 ppm，SPS：10 ppm，JGB：10 ppm）

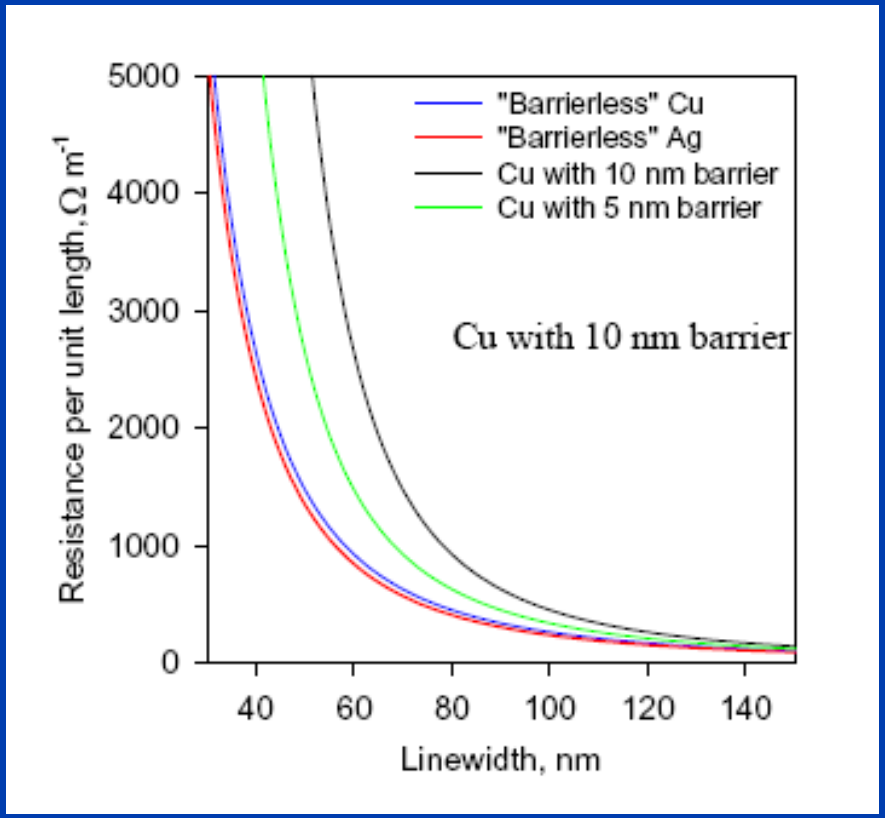


Source:
Prof. Osaka
Waseda U.

Anneal is needed to stabilize the film (grain size, roughness, resistivity, texture, etc)

Cu Resistivity Scaling





In Summary

- A chemical mechanism for Cu electroplating is proposed
  - bottom up fill in trenches/vias is explained by accumulation of ACCELERATOR (ASUPP) at the bottom of features which reduces effect of SUPPRESSOR (SUPP)
- Electrochemical methods (CVS and LSV) were reviewed to study additives
- Bath stability can be maintained by using
  - auto-replenishment of plating bath ingredients with on-line bath analysis with p/t <0.3
- Defects and Uniformity can be reduced by using additives and optimizing plating reactor
- Electroplating conditions can be optimized to achieve
  - (111) textured Cu films with large grain size, significant fraction of twin grain boundaries, and controlled impurities content